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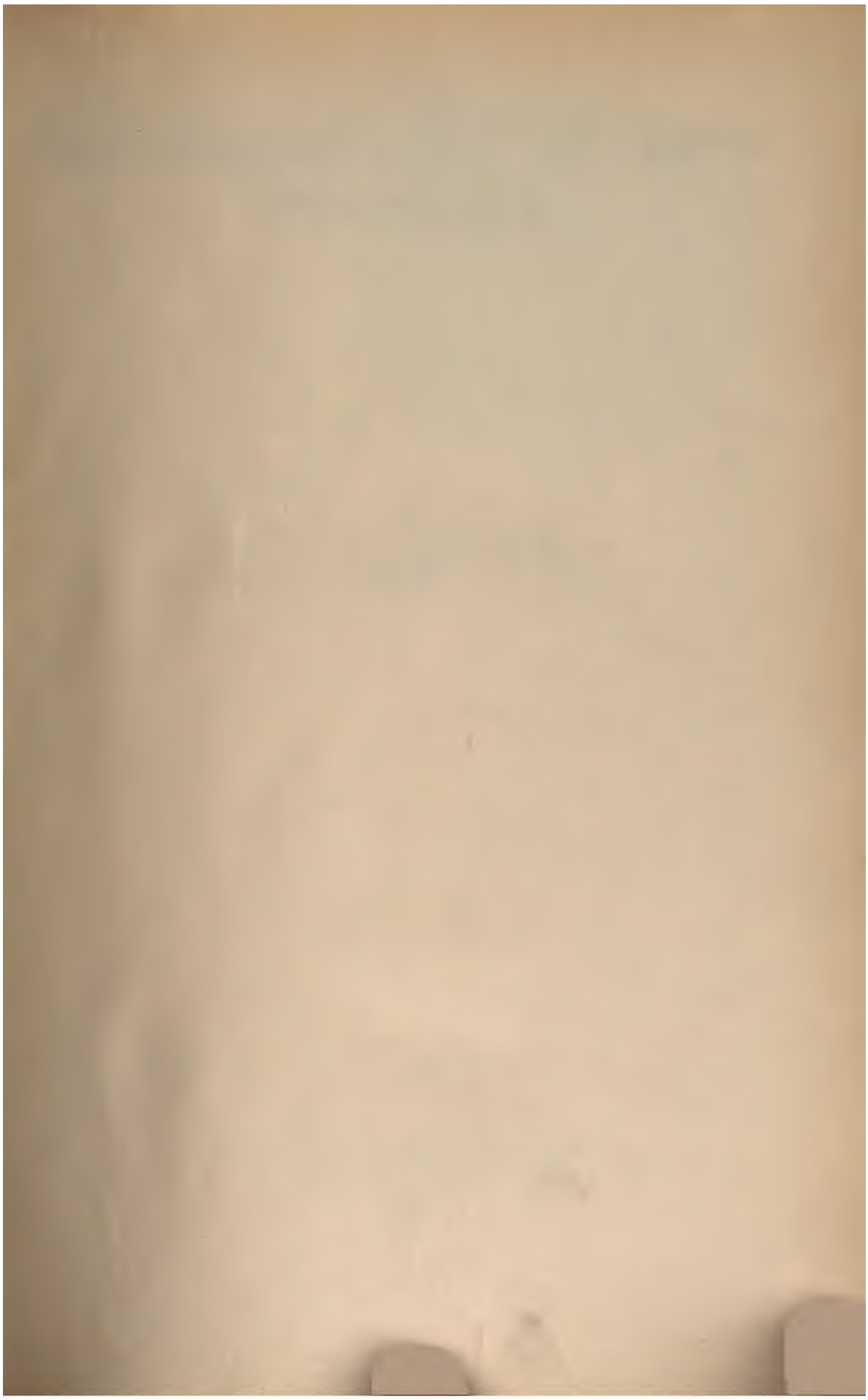

THE METALLOGRAPHY OF IRON AND STEEL

BY

ALBERT SAUVEUR

Professor of Metallurgy and Metallography in Harvard University

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TO
THE MEMORY OF
My Father
I REVERENTLY AND LOVINGLY
DEDICATE THIS BOOK

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PREFACE

WHILE several excellent books on metallography have been published and while numerous papers on the metallography of iron and steel have appeared in the scientific and technical press, a well-balanced, specific, and comprehensive treatise on the subject has not heretofore been written. In the belief that there is a real and urgent need of such a treatise the author has endeavored to supply it, craving for his effort the indulgent criticism of his readers. He offers his book to those seeking self-instruction in the metallography of iron and steel, their special needs having been carefully considered in the arrangement of the lessons; he offers it to teachers and students trusting that they will find it valuable and suggestive as a text-book; he offers it to manufacturers and users of iron and steel in the belief that he has given due weight to the practical side of the subject and has avoided discussions of ill-founded or purely speculative theories; he offers it to the general reader interested in the scientific or practical features of the metallography of iron and steel, as the language used should be readily understood by those lacking specialized knowledge of the subject; he offers it to experts in the hope that they will find it not entirely devoid of original thought, original treatment, and suggestiveness.

In the matter of illustrations and especially of photomicrographs the author's aim has been to utilize the best available, using his own or those taken in his laboratory only when no better ones have, to his knowledge, been published by others. The original source of every illustration has been indicated and the author desires to express his indebtedness to the following writers, the figures in parenthesis showing the number of illustrations from each: Andrews (3), Arnold (7), Bayley (1), Belaiew (5), Brearley (2), Carpenter and Keeling (1), Sherard Cowper-Coles (1), Desch (4), Edwards (2), Ewing and Rosenhain (2), Guillet (18), Gœrens (9), Gulliver (2), Hall (1), Houghton (1), Kroll (1), Law (8), Levy (1), Longmuir (2), Matweieff (1), Maurer (1), Mellor (1), Osmond (17), Roberts-Austen (1), Robin (1), Roland-Gosselin (1), Rosenhain (2), Saladin (2), Sorby (1), Stead (13), Tschermak (5), Tschernoff (1), Wüst (5), Ziegler (1). All illustrations not otherwise inscribed are the author's.

The author cannot refrain from expressing here the sorrow and sense of personal loss he experienced when the news was received, while this book was passing through the press, of the death of Floris Osmond, for to the author, as no doubt to many others, Osmond's work and Osmond's life have been an inspiration. Osmond belonged to that admirable class of French scientists, who, like Pasteur and Berthelot, have so lofty a conception of the duty of the scientist that they give to the world the fruit of

their genius and of their untiring labors with no thought of monetary return or even of honorary recognition. If Sorby was the pioneer of metallography and Tschernoff its father, Osmond has been its torch-bearer for he, more than any other, has been our guide. While he is no longer with us, his light will long continue to burn and to show the way to promising and productive fields of research.

The author desires to place on record his warm appreciation of the assistance he received from Mr. H. M. Boylston in passing this book through the press, and also for many valuable suggestions.

ALBERT SAUVEUR.

HARVARD UNIVERSITY,
CAMBRIDGE, MASSACHUSETTS,
August 19, 1912.

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TABLE OF CONTENTS

INTRODUCTION

PAGE

THE INDUSTRIAL IMPORTANCE OF METALLOGRAPHY 1

APPARATUS FOR THE METALLOGRAPHIC LABORATORY

THE MICROSCOPE 1
The stage 1
Plain stages 3
Mechanical stages 3
Objectives 3
Eye-pieces 3
Iris diaphragms 7
Specimen holders 7
UNIVERSAL METALLOSCOPE 10
Electromagnetic stage 11
Templets for the examination of small specimens 11
Support of non-magnetic specimens 11
Leveling-devices of stand and stage 12
Motion of the stage 12
Mechanical stage 12
Examination of transparent objects 13
ILLUMINATION OF THE SAMPLES 14
SOURCES OF LIGHT AND CONDENSERS 18
Monochromatic light 22
PHOTOMICROGRAPHIC CAMERAS 22
INVERTED MICROSCOPES 28
POLISHING APPARATUS 28
Hand polishing 28
Polishing by power 30
PYROMETERS AND ELECTRIC FURNACES 30
Pyrometers 30
Electric Furnaces 35

LESSON I — PURE METALS

Microstructure 1
Crystallization 1
Idiomorphic crystals 2
Allotrimorphic crystals 2
Crystallization of metals 2
Grains of metals 3
Crystalline orientation of the grains 3
Cubic crystallization of metals. — Etching pits 4
Summary 4
Impurities 5
Influence of thermal treatment 7
Influence of mechanical treatment 8
Examination 8

LESSON II — PURE IRON

PAGE

Microstructure 1
Cubic crystallization of iron 2
Ferrite 4
Allotropy of iron 4
Influence of impurities 10
Influence of heat treatment 10
Influence of mechanical treatment 11
Straining of iron. — Slip bands 11
Examination 12

LESSON III — WROUGHT IRON

Chemical composition 1
Microstructure of longitudinal section 1
Microstructure of transverse section 2
Chemical composition of slag 3
Microstructure of slag 3
Influence of thermal and mechanical treatments 4
Experiments 4
Polishing by hand 4
Polishing by power 6
Etching 6
Etching with picric acid 6
Examination 7
Etching with diluted nitric acid 7
Etching with concentrated nitric acid 8
Examination 8

LESSON IV — LOW CARBON STEEL

Normal structure 1
Grading of steel vs. carbon content 1
Low carbon steel vs. wrought iron 1
The structure of low carbon steel 2
Pearlite 3
Free ferrite 4
Cementite 5
Experiments 5
Polishing 5
Etching 6
Photomicrography 6
Exposure 7
Diaphragms and shutters 7
Monochromatic light 7
Photographic plates 8
Development 8
Printing 8
Mounting 8
Examination 8

LESSON V — MEDIUM HIGH AND HIGH CARBON STEEL

Medium high carbon steel 1
High carbon steel 4
Eutectoid steel 4

PAGE

Hyper-eutectoid steel 4
Free cementite 5
Hypo- vs. hyper-eutectoid steel 6
Etching of cementite 7
Carbon content of pearlite 8
Structural composition of steel 8
Chemical vs. structural composition 11
Micro-test for determination of carbon in steel 12
Physical properties of the constituents of steel 14
Tenacity of steel vs. its structural composition 15
Steel of maximum strength 17
Ductility of steel vs. its structural composition 17
Diagram showing the relation between the tenacity and ductility of steel and its carbon content 19
Experiments 19
Etching 19
Etching with sodium picrate 19
Photomicrography 19
Examination 20

LESSON VI — IMPURITIES IN STEEL

Metallic impurities 1
Non-metallic or oxidized impurities 1
Metallic vs. non-metallic impurities 1
Gaseous impurities 1
Impurities vs. physical properties of steel 1
Silicon in steel 1
Phosphorus in steel 2
Sulphur in steel 2
Manganese in steel 5
Chemical vs. structural composition 6
Non-metallic or oxidized impurities 8
Gaseous impurities 9
Segregation of impurities. — Ghosts 10
Experiments 11
High vs. low phosphorus steel 11
High sulphur steel 12
Oxidized Bessemer metal 12
Segregated steel 12
Examination 12

LESSON VII — THE THERMAL CRITICAL POINTS OF IRON AND STEEL

THEIR OCCURRENCE

Point of recalescence 1
Notation 2
Critical range. — Transformation range 2
Position of Ar_1 and Ac_1 2
Speed of cooling and heating vs. position of A_1 4
Chemical composition vs. position of A_1 5
Upper critical points 5
Thermal critical points in pure iron 5
Thermal critical points in very low carbon steel 6
Peculiarities of the point A_2 6
Thermal critical points of medium high carbon steel 6
Merging of A_3 and A_2 6
Thermal critical points in eutectoid steel 7

539455

PAGE

Merging of $A_{3\text{-}2}$ and A_1 . . . 7
Thermal critical points in hyper-eutectoid steel . . . 7
Merging of $A_{3\text{-}2\text{-}1}$ and A_{cm} . . . 8
Minor critical points . . . 8
Data showing the position of the critical points . . . 8
Relative quantities of heat evolved or absorbed at the critical points . . . 8
Graphical representation of the position and magnitude of the critical points . . . 10
Determination of the thermal critical points . . . 10
Cooling and heating curves . . . 10
Use of neutral bodies . . . 14
Additional illustrations of cooling curves . . . 18
Self-recording pyrometers . . . 18
Historical . . . 19
Experiments . . . 19
Examination . . . 20

LESSON VIII — THE THERMAL CRITICAL POINTS OF IRON AND STEEL

THEIR CAUSES

Causes of the upper points A_3 and A_2 in carbonless iron . . . 1
Causes of the upper critical points A_3 and A_2 in low carbon steel . . . 3
Cause of the point $A_{3\text{-}2}$ . . . 4
Cause of the point A_1 . . . 4
The point A_1 an allotropic point . . . 6
Pearlite formation . . . 7
Cause of the point A_{cm} . . . 7
Allotropy of cementite . . . 9
Cause of the point $A_{3\text{-}2\text{-}1}$ in eutectoid steel . . . 9
Cause of the point $A_{3\text{-}2\text{-}1}$ in hyper-eutectoid steel . . . 11
Formation of beta iron . . . 11
Summary . . . 11
Another view of the allotropic changes . . . 14
Examination . . . 16

LESSON IX — THE THERMAL CRITICAL POINTS OF IRON AND STEEL

THEIR EFFECTS

Changes at A_3 . . . 1
- Dilatation . . . 1
- Electrical conductivity . . . 1
- Crystallization . . . 2
- Hardness, ductility, strength . . . 2
- Dissolving power for carbon . . . 2
- Structural properties . . . 3
- Other properties . . . 3

Changes at A_2 . . . 3
- Dilatation . . . 3
- Magnetic properties . . . 3
- Crystallization . . . 5
- Hardness, ductility, strength . . . 5
- Dissolving power for carbon . . . 5
- Structural properties . . . 5
- Other properties . . . 6

Changes at $A_{3\text{-}2}$ . . . 6
Changes at A_1 . . . 6
Changes at $A_{3\text{-}2\text{-}1}$ . . . 6
Changes at A_{cm} . . . 7

PAGE
Structural change at A_1 and $A_{3\text{-}2\text{-}1}$ 7
Prevailing conditions above and below the critical range 7
Properties of gamma, beta, and alpha iron 8
Examination 8

LESSON X — CAST STEEL

Structure of cast eutectoid steel 1
Structure of cast hypo-eutectoid steel 2
Structure of cast eutectoid vs. cast hypo-eutectoid steel 3
Structure of cast hyper-eutectoid steel 4
Ingotism 5
Structure of cast steel vs. structure of meteorites 6
Octahedric crystallization of austenite 7
Experiments 10
Examination 10

LESSON XI — THE MECHANICAL TREATMENT OF STEEL

Hot working 1
Finishing temperatures 3
Structure of hot worked eutectoid steel 4
Structure of hot worked hypo-eutectoid steel 4
Structure of hot worked hyper-eutectoid steel 6
Sorbite 6
Hot working of steel vs. its critical range 7
Cold working 8
Mechanical refining 9
Experiments 10
Examination 10

LESSON XII — THE ANNEALING OF STEEL

Purpose of annealing 1
Nature of the annealing operation 1
Heating for annealing 1
Time at annealing temperature 2
Cooling from annealing temperature 2
Rate of cooling vs. carbon content 3
Rate of cooling vs. size of object 3
Furnace cooling from annealing temperature 4
Air cooling from annealing temperature 4
Properties of sorbite 5
Influence of maximum temperature 5
Influence of time at maximum temperature 6
Oil and water quenching from annealing temperature 6
Double annealing treatment 8
Annealing eutectoid steel 10
Annealing hypo-eutectoid steel 11
Annealing hyper-eutectoid steel 12
Annealing steel castings 13
Spheroidizing of pearlite-cementite 14
Varieties of pearlite 15
Graphitizing of cementite 15
Burnt steel 17
Crystalline growth of austenite above the critical range 20
Crystalline growth of ferrite below the critical range 23

PAGE

Brittleness of low carbon steel 26
Experiments 29
Examination 29

LESSON XIII — THE HARDENING OF STEEL

Heating for hardening 1
Cooling for hardening 1
Structural changes on hardening 2
Austenite 3
Nature of austenite 3
Occurrence of austenite 4
Etching of austenite 6
Structure of austenite 7
Properties of austenite 7
Martensite 10
Nature of martensite 10
Occurrence of martensite 10
Etching of martensite 10
Structure of martensite 11
Properties of martensite 11
Troostite 11
Nature of troostite 11
Occurrence of troostite 12
Properties of troostite 13
Etching of troostite 13
Structure of troostite 13
Sorbite 13
Troosto-sorbite 15
Hardenite 15
Rate of cooling through critical range vs. structure of steel 15
Are the transition stages distinct constituents? 17
Metarals and aggregates 18
Hardening eutectoid steel 18
Hardening hyper-eutectoid steel 18
Hardening hypo-eutectoid steel 18
Steel of maximum hardening power 20
Hardening large pieces 20
Hardening and tempering in one operation 20
Experiments 20
Etching 21
Examination 21

LESSON XIV — THE TEMPERING OF HARDENED STEEL

Tempering temperatures 1
Tempering colors 1
Time at tempering temperature 1
Rate of cooling from tempering temperature 2
Hardening and tempering combined 2
Explanation of the tempering of steel 2
Tempering austenitic steels 3
Tempering martensitic steel 5
Tempering troostitic steel 5
Tempering troosto-martensitic steel 5
Tempering troosto-sorbitic steel 5
Osmondite 5
Structural changes on slow cooling, quick cooling, and reheating 7

PAGE

Microstructure of hardened and tempered steel 7
Carbon condition in tempered steel 8
Decrease of hardness on tempering 9
Heat liberated on tempering 9
Experiments 10
Examination 10

LESSON XV — THEORIES OF THE HARDENING OF STEEL

Retention theories 1
Solution theories 2
Gamma iron theory 2
Beta iron or allotropic theory 2
Alpha iron theory 4
Carbon theories 4
The hardening carbon theory 4
The subcarbide theory 4
The stress theory 5
Tempering and the retention theories 6
Tempering and the stress theory 6
Summary 6
Examination 7

LESSON XVI — THE CEMENTATION AND CASE HARDENING OF STEEL

Composition of the iron and steel subjected to carburizing 1
Carburizing temperature 1
Time at carburizing temperature 2
Distribution of the carbon 2
Carburizing materials 4
Mechanism of cementation 5
Cooling from carburizing temperature 5
Heat treatment of case hardened articles 5
Tempering case hardened steel 6
Experiments 6
Examination 6

LESSON XVII — SPECIAL STEELS

GENERAL CONSIDERATIONS

Ternary steels 1
Influence of the special element upon the location of the critical range 3
Pearlitic steels 6
Martensitic steels 7
Austenitic (polyhedric) steels 7
Cementitic (carbide) steels 8
Treatments of special steels 8
Treatment of pearlitic steels 8
Treatment of martensitic steels 9
Treatment of austenitic steels 9
Treatment of cementitic steels 9
Quaternary steels 10
Examination 10

LESSON XVIII — SPECIAL STEELS

CONSTITUTION, PROPERTIES, TREATMENT, AND USES OF MOST IMPORTANT TYPES

Nickel steel 1
Manganese steel 5
Tungsten steels 12

PAGE

Chrome steels . . . 13
Vanadium steels . . . 15
Silicon steels . . . 15
Chrome-nickel steels . . . 16
Quaternary vanadium steels . . . 17
Chrome-tungsten or high-speed steels . . . 17
Experiments . . . 20
Examination . . . 20

LESSON XIX — CAST IRON

Formation of combined and graphitic carbon . . . 1
Cast iron containing only graphitic carbon . . . 1
Cast iron containing only combined carbon . . . 3
Cast iron containing both combined and graphitic carbon . . . 8
Mottled cast iron . . . 10
Structural composition of cast iron . . . 10
Physical properties of cast iron vs. its structural composition . . . 11
Chilled cast iron castings . . . 13
Examination . . . 13

LESSON XX — IMPURITIES IN CAST IRON

Silicon in cast iron . . . 1
Sulphur in cast iron . . . 1
Manganese in cast iron . . . 2
Phosphorus in cast iron . . . 2
Structural composition of phosphoretic cast iron . . . 7
Chemical vs. structural composition . . . 8
Experiments . . . 9
Examination . . . 9

LESSON XXI — MALLEABLE CAST IRON

Graphitizing of cementite . . . 1
Malleable cast-iron castings . . . 1
Original castings . . . 2
Annealing operation . . . 3
Packing materials . . . 3
Annealing for malleablizing . . . 4
Annealing for " white heart " castings . . . 4
Annealing for " black heart " castings . . . 5
Gray cast iron vs. malleable cast iron . . . 7
Experiments . . . 8
Examination . . . 8

LESSON XXII — CONSTITUTION OF METALLIC ALLOYS

Solidification of pure metals . . . 1
Solidification of binary alloys the constituents of which form solid solutions . . . 3
Fusibility curves of binary alloys whose component metals are completely soluble in each other when solid . . . 5
Binary alloys forming definite compounds and solid solutions . . . 8
Binary alloys whose component metals are insoluble in each other in the solid state . . . 9
Binary alloys whose component metals are partially soluble in each other when solid . . . 17
Examination . . . 21

LESSON XXIII — EQUILIBRIUM DIAGRAM OF IRON-CARBON ALLOYS

PAGE
Fusibility curve of iron-carbon alloys . . . 1
Structural composition of iron-carbon alloys immediately after solidification . . . 3
Iron-graphite fusibility curve . . . 7
Combined graphite-cementite diagram . . . 7
Graphitizing of cementite . . . 7
Structure of iron-carbon alloys immediately after solidification . . . 10
Complete equilibrium diagram . . . 12
Historical . . . 16
Examination . . . 21

LESSON XXIV — THE PHASE RULE

Enunciation of the phase rule . . . 1
Equilibrium . . . 1
Degrees of freedom . . . 2
Phases . . . 3
Components . . . 3
The phase rule applied to alloys . . . 3
The phase rule applied to pure metals . . . 4
The phase rule applied to binary alloys . . . 4
The phase rule applied to iron-carbon alloys . . . 6
Examination . . . 8

APPENDIX I — MANIPULATIONS AND APPARATUS

Polishing and Polishing Machines . . . 1
Development of the Structures . . . 9
Polishing in relief . . . 9
Polish-attack . . . 9
Etching . . . 10
Electrolytic etching . . . 11
Heat tinting . . . 11
Hot etching . . . 11
Washing and drying . . . 11
Preserving . . . 12
Mounting and Mounting Devices . . . 12
Plastic mountings . . . 12
Leveling stages . . . 14
Metallurgical Microscopes . . . 16

APPENDIX II — NOMENCLATURE OF THE MICROSCOPIC CONSTITUENTS

I. General Plan . . . 1
II. List of Microscopic Substances . . . 2
III. Definitions and Descriptions . . . 4
Austenite . . . 4
Cementite . . . 6
Martensite . . . 7
Ferrite . . . 7
Osmondite . . . 8
Ferronite . . . 9
Hardenite . . . 9
Pearlite . . . 9
Graphite . . . 10

III. DEFINITIONS AND DESCRIPTIONS — *continued* PAGE
Troostite 11
Sorbite 11
Manganese sulphide 12
Ferrous sulphide 12
MISCELLANEOUS 12

INDEX 1–15

ERRATA

Lesson IV, page 5, fifth paragraph, line 3, for "an iron carbide Mn_3C" read "a carbide Mn_3C."

Lesson V, page 4, second paragraph, line 3, for "euctectic" read "eutectic."

Lesson V, page 9, the first two equations should read
"F = per cent free ferrite = 41.18
P = per cent pearlite = 58.82"

Lesson V, page 16, instead of "T = 1250 P + 100 (50 − P)"
the third equation should read
"T = 1250 P + 50 (100 − P)"

instead of "T = 5000 + 1150 P"
the fourth equation should read
"T = 5000 + 1200 P"

instead of "$T = 5000 + 1150 \frac{800 - 120\,C}{7}$"
the sixth equation should read
"$T = 5000 + 1200 \frac{800 - 120\,C}{7}$"

instead of "$T = \frac{955{,}000 - 138{,}000\,C}{7}$"
the seventh equation should read
"$T = \frac{995{,}000 - 144{,}000\,C}{7}$"

instead of "T = 136,000 − 20,000 C."
the eighth equation should read
"T = 142,000 − 20,600 C."

last line, instead of "111,000" read "116,250"
instead of "106,000" read "111,100"

Lesson V, page 17, last line of footnote, for "allow heat treatment" read "allow for heat treatment."

Lesson X, page 6, eighth line from the bottom, for "peroid" read "period."

Lesson XV, page 6, next to last line, last word, for "carbon" read "iron."

INTRODUCTION

THE INDUSTRIAL IMPORTANCE OF METALLOGRAPHY[1]

Twenty years ago the science of metallography was practically unknown and it is only within the last fifteen years that it has been seriously considered by metal manufacturers and consumers as a valuable method of testing and investigating. That so much has been accomplished in so short a time is highly gratifying to the many workers, practical or scientific, who have contributed by their efforts to the progress of metallography.

To realize the practical importance of metallography it should be borne in mind that the physical properties of metals and alloys — that is, those properties to which these substances owe their exceptional industrial importance — are much more closely related to their proximate than to their ultimate composition, and that microscopical examination reveals, in part at least, the proximate composition of metals and alloys, whereas chemical analysis seldom does more than reveal their ultimate composition.

It will bear repeating that from the knowledge of the proximate composition of a certain industrial metal or alloy we are able to infer its properties and, therefore, predict its adaptability with a much greater degree of accuracy than if we knew only its ultimate composition.

The analytical chemist may tell us, for instance, that a steel which he has analyzed contains 0.50 per cent of carbon, without our being able to form any idea as to its properties, for such steel may have a tenacity of some 75,000 lbs. per square inch or of some 200,000 lbs., a ductility represented by an elongation of some 25 per cent, or practically no ductility at all; it may be so hard that it cannot be filed or so soft as to be easily machined, etc.

The metal microscopist, on the contrary, on examining the same steel will report its structural, i.e. its proximate, composition, informing us that it contains, for instance, approximately 50 per cent of ferrite and 50 per cent of pearlite, and we know at once that the steel is fairly soft, ductile, and tenacious; or he may report the presence of 100 per cent of martensite, and we know that the steel is extremely hard, very tenacious, and deprived of ductility.

Which of the two reports is of more immediate practical value, the chemist's or the metallographist's? Surely, that of the metallographist.

Nor is it only in the domain of metals that we find such close relationship between properties and proximate composition, for, on the contrary, it is quite true of all substances. How many organic bodies, for instance, have practically the same ultimate composition and still are totally unlike in properties because of their different proximate composition, i.e. different grouping and association of their ultimate con-

[1] Abstracted from a paper presented at the Congress of Technology at the fiftieth anniversary of the granting of the charter of the Massachusetts Institute of Technology.

stituents. If we were better acquainted with the proximate composition of substances many unexplained facts would become clear to us.

Unfortunately the chemist too often is able to give us positive information in regard to the proportion of the ultimate constituents only, his reference to proximate analysis being of the nature of speculation. Ultimate analysis has reached a high degree of perfection in regard to accuracy as well as to speed of methods and analytical chemists have built up a marvelous structure calling for the greatest admiration, their searching methods never failing to lay bare the ultimate composition of substances. But how much darkness still surrounds the proximate composition of bodies and how great the reward awaiting the lifting of the veil!

The forceful and prophetic writing in 1890 of Prof. Henry M. Howe naturally comes to mind. Speaking of the properties and constitution of steel, Professor Howe wrote:

"If these views be correct, then, no matter how accurate and extended our knowledge of ultimate composition, and how vast the statistics on which our inferences are based, if we attempt to predict mechanical properties from them accurately we become metallurgical Wigginses . . .

"Ultimate analysis never will, proximate analysis may, but by methods which are not yet even guessed at, and in the face of fearful obstacles.

"How often do we look for the coming of the master mind which can decipher our undecipherable results and solve our insoluble equations, while if we will but rub our own dull eyes and glance from the petty details of our phenomena to their great outlines their meaning stands forth unmistakably; they tell us that we have followed false clues and paths which lead but to terminal morasses. In vain we flounder in the sloughs and quagmires at the foot of the rugged mountain of knowledge seeking a royal road to its summit. If we are to climb, it must be by the precipitous paths of proximate analysis, and the sooner we are armed and shod for the ascent, the sooner we devise weapons for this arduous task, the better.

"By what methods ultimate composition is to be determined is for the chemist rather than the metallurgist to discover. But, if we may take a leaf from lithology, if we can sufficiently comminute our metal (ay, there's the rub!) by observing differences in specific gravity (as in ore dressing), in rate of solubility under rigidly fixed conditions, in degree of attraction by the magnet, in cleavage, luster, and crystalline form under the microscope, in readiness of oxidation by mixtures of gases in rigidly fixed proportions, we may learn much.

"Will the game be worth the candle? Given the proximate composition, will not the mechanical properties of the metal be so greatly influenced by slight and undeterminable changes in the crystalline form, size, and arrangement of the component minerals, so dependent on trifling variations in manufacture as to be still only roughly deducible?"

The above was written before the days of metallography, or at least when metallography had barely appeared in the metallurgical sky and when no one yet had fancied what would be the brilliant career of the newcomer. Metallography has done much to supply the need so vividly and timely depicted by Professor Howe, precisely because by lifting a corner of the veil hiding from our view the proximate composition of metals and alloys it has thrown a flood of light upon the real constitution of these important products. Has the game been worth the candle? Will any one hesitate to answer in the affirmative Professor Howe's question?

Professor Howe with his usual acumen was conscious of the fact that proximate analysis, while likely to reveal a great deal more of the constitution of metals than ultimate analysis ever could, might still leave us in such ignorance of their physical structure as to throw but little additional light upon the subject. His fear was certainly well founded and surely if the proximate composition had been obtained by chemical analysis it would indeed have told us little of the structure or anatomy of the metals. In the domain of proximate composition chemistry cannot do more for the metallurgist than it does for the physician.

Invaluable information chemistry does give, without which both the physician and the metallurgist would be in utter darkness, but it throws little or no light upon the anatomy of living or inanimate matter. Its very methods which call for the destruction of the physical structure of matter show how incapable it is to render assistance in this, our great need.

The parallel drawn here between metals and living matter is not fantastic. It has been aptly made by Osmond, who said rightly that modern science was treating the industrial metal like a living organism and that we were led to study its anatomy, i.e. its physical and chemical constitution; its biology, i.e. the influence exerted upon its constitution by the various treatments, thermal and mechanical, to which the metal is lawfully subjected; and its pathology, i.e. the action of impurities and defective treatments upon its normal constitution.

Fortunately metallography does more than reveal the proximate composition of metals. It is a true dissecting method which lays bare their anatomy — that is, the physical grouping of the proximate constituents, their distribution, relative dimensions, etc., all of which necessarily affect the properties. For two pieces of steel, for instance, might have exactly the same proximate composition — that is, might contain, let us say, the same proportion of pearlite and ferrite and still differ quite a little as to strength, ductility, etc., and that because of a different structural arrangement of the two proximate constituents; in other words, because of unlike anatomy.

It is not to be supposed that the path trodden during the last score of years was at all times smooth and free from obstacles. Indeed, the truth of the proverb that there is no royal road to knowledge was constantly and forcibly impressed on the mind of those engaged in the arduous task of lifting metallography to a higher level.

Its short history resembles the history of the development of all sciences. At the outset a mist so thick surrounds the goal that only the most courageous and better equipped attempt to pierce it and perchance they may be rewarded by a gleam of light. This gives courage to others and the new recruits add strength to the besieging party. Then follows the well-known attacking methods of scientific tactics and strategy, and after many defeats and now and then a victorious battle the goal is in sight, but only in sight and never to be actually reached, for in our way stands the great universal mystery of nature: what is matter? what is life?

Nevertheless there is reward enough for the scientist in the feeling that he has approached the goal, that he has secured a better point of vantage from which to contemplate it. The game was worth the candle. And if scientific workers must necessarily fail in their efforts to arrive at the true definition of matter, whatever be the field of their labor, they at least learn a great deal concerning the *ways of matter*, and it is with the ways of matter that the material world is chiefly concerned. Hence the usefulness of scientific investigation, hence the usefulness of metallography.

Like any other science with any claim to commercial recognition, metallography

has had first to withstand the attack and later to overcome the ill-will and reluctance of the so-called "practical man" with a decided contempt for anything scientific. He represents the industrial philistine clumsily standing in the way of scientific applications to industrial operations. Fortunately, while his interference may retard progress, it cannot prevent it. Had he had his own way neither the testing machine, nor the chemical laboratory, nor the metallographical laboratory, nor the pyrometer would ever have been introduced in iron and steel works.

Speaking in 1904 of the practical value of metallography in iron and steel making, the author wrote the following, which it may not be out of place to reproduce here: "History, however, must repeat itself, and the evolution of the metallographist bids fair to be an exact duplicate of the evolution of the iron chemist; the same landmarks indicate his course; distrust, reluctant acceptance, unreasonable and foolish expectation from his work, disappointment because these expectations were not fulfilled and finally the finding of his proper sphere and recognition of his worth. The metallographist has passed through the first three stages of this evolution, is emerging from the fourth, and entering into the last. For so young a candidate to recognition in iron and steel making this record is on the whole very creditable."

We may say to-day that he has definitely entered the last stage and that the adverse criticisms still heard from time to time, generally from the pen or mouth of ignorant persons, are like the desultory firing of a defeated and retreating enemy.

In the United States alone the microscope is in daily use for the examination of metals and alloys in more than two hundred laboratories of large industrial firms, while metallography is taught in practically every scientific or technical school.

A. S.

HARVARD UNIVERSITY,
February, 1912.

APPARATUS FOR THE METALLOGRAPHIC LABORATORY.[1]

Only those apparatus which the author has found most satisfactory are here mentioned — other instruments will be found described in an Appendix.

THE MICROSCOPE

While any good microscope of the ordinary type, substantially built and provided with a satisfactory fine adjustment, may be used with a certain degree of success for the examination of metals and alloys, those who are restricted to its use will soon find themselves seriously handicapped in several directions and unable to obtain the desired results. The following considerations will make this clear.

The Stage. — Ordinary microscope stands being constructed for the examination of objects by transmitted light, i.e. by light proceeding from below the stage and passing through the object on its way to the eye, are provided with fixed stages. This, however, is a serious objection when the instrument is applied to the examination of metals and other opaque objects which must necessarily be illuminated by light directed upon them from *above* the stage, and which therefore require the use of an " illuminator " attached to the objective and consequently moving with it. It will be readily understood that it is of considerable importance that the position of this illuminator, and therefore of the objective to which it is attached, be kept constant, once the necessary adjustments are effected, since any change in its position would require a readjustment of the source of light, the condensing lenses, diaphragm, etc. To that effect the stage should be provided with a rack and pinion motion by means of which the coarse focusing at least may be done (Fig. 1).

This rack and pinion motion of the stage, moreover, permits of a much greater working distance, allowing plenty of room for the insertion of the illuminator and nose-piece, the use of specimen holders, and the examination of bulky specimens with low-power objectives. In the microscope illustrated in Figure 1, the working distance measures over 5 inches as against 4 inches or less in ordinary stands.

By not departing more than necessary from the usual construction of microscopes, none of the essential features required for the examination of transparent preparations need be sacrificed, and the full efficiency of the microscope is retained for such examination, sub-stage condensers, polarizing prisms, etc., being readily attached when needed. The possibility of applying his instrument to all kinds of microscopical work with equally satisfactory results should appeal strongly to the metallographist, for there is no laboratory where, occasionally at least, examination of transparent objects is not desirable or even imperative.

[1] Abstracted in part from papers by the author on "Apparatus for the Microscopical Examination of Metals," American Society for Testing Materials, Vol. X, 1910; and "The Universal Metalloscope," American Institute of Mining Engineers, June, 1911.

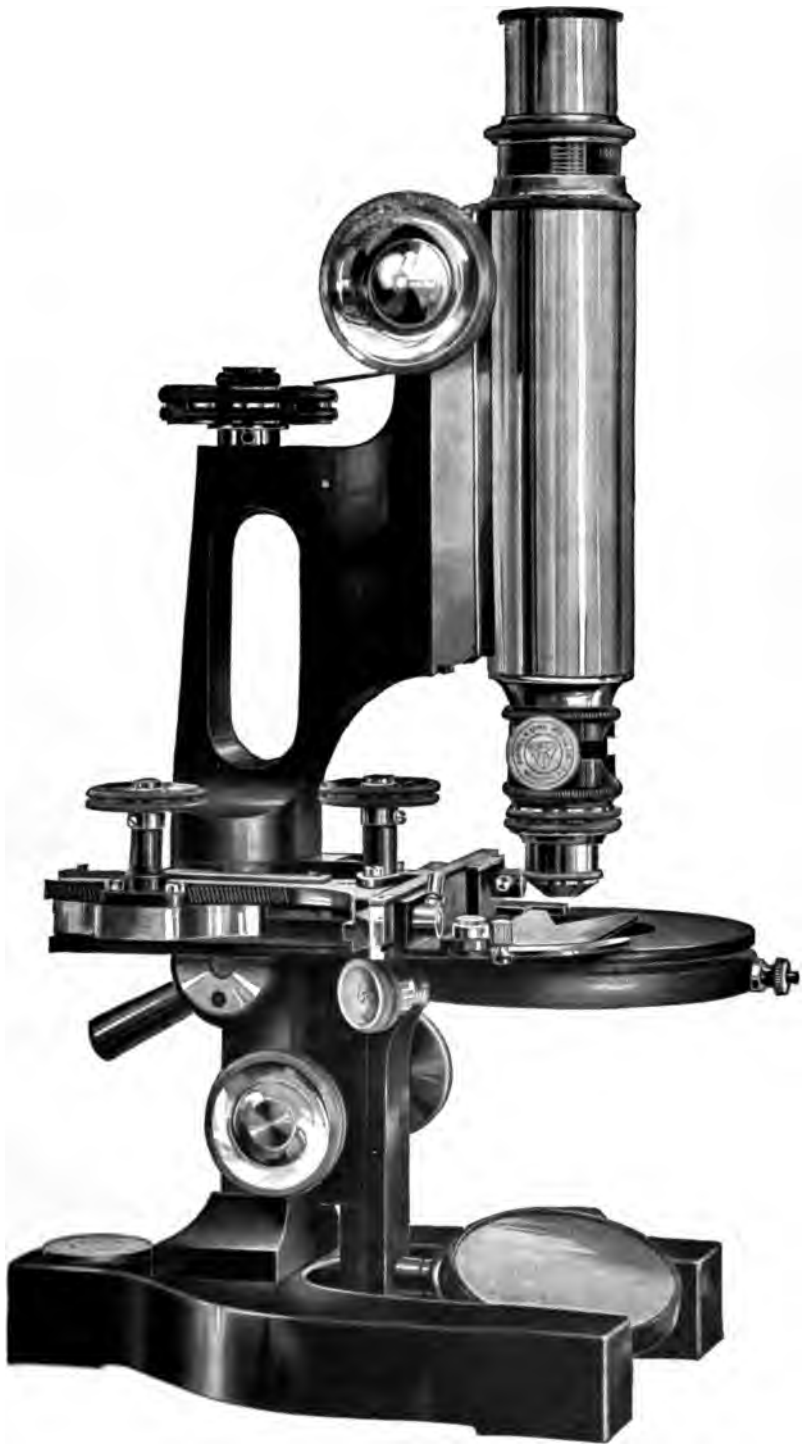


Fig. 1. Metallurgical microscope, eye-piece, vertical illuminator, objective, magnetic specimen holder, and mechanical stage.

A less expensive but satisfactory microscope is shown in Figures 2 and 3. The latter illustration includes an auxiliary tube inserted between the objective and illuminator for the examination of large samples which may be placed on the base of the microscope or supported in some other suitable way below the stage.

(*a*) *Plain Stages.* — While a mechanical stage adds greatly to the convenience of the manipulations, a plain stage may be used with satisfactory results. It should be provided with strong clips to hold in place the specimen holders soon to be described, and should preferably be circular and revolving (Fig. 4). When provided with centering screws like the stage of the stand illustrated in Figure 1, the object may be moved gently while under examination, a very desirable feature especially when using high-power objectives, in which case the moving of the object entirely by hand is very jerky. In order to derive the full benefit of the use of the magnetic holder described later, the central opening of the stage should not be less than $1\frac{1}{4}$ inches in diameter.

(*b*) *Mechanical Stages.* — The great superiority of a mechanical stage permitting, as it does, a systematic examination of the object over its entire surface, need not be insisted upon. In connection with the magnetic holder it makes it possible, moreover, to examine repeatedly and at any time the same spot of any specimen, as will soon be explained. The mechanical stage illustrated in Figure 5 has been especially designed to fit the metallurgical microscope (Fig. 1), and is very readily substituted for the plain stage. The central opening measures $1\frac{5}{8}$ inches in diameter, permitting the convenient use of the magnetic holder.

Objectives. — Ordinary achromatic objectives give satisfactory results. They should, however, be corrected for uncovered objects, as the placing of cover glasses over bright metallic surfaces is accompanied by light reflection causing loss of clearness and definition.

Some believe that the objectives should be provided with short mounts so as to bring the reflector of the vertical illuminator as near the back lens of the objective as possible, and thus, in their opinion, materially decreasing the amount of glare caused by the reflection of light by the lenses of the objectives. Three objectives, one of low, one of medium, and one of high power, will generally suffice for metallographic work. The following focal lengths are recommended: 32-mm. or $1\frac{1}{3}$-in., 16-mm. or $\frac{2}{3}$-in., and 4-mm. or $\frac{1}{6}$-in. These objectives are shown, in short mounts, in Figure 6. The 32-mm. objective is provided with a society screw at its lower end in order that the vertical illuminator may be inserted between the objective and the object, this being desirable with very low-power lenses. In case a higher power is needed, a 2-mm. or $\frac{1}{12}$-in. oil immersion objective will be found very satisfactory. When a very low-power lens is required, as for instance in the examination of fractures or of very coarse structures, a 48-mm. or 2-in. objective will give good results. It is suggested that it be provided at its lower end with a society screw to permit the attachment of the vertical illuminator, which in the case of such low-power lenses should be placed between the object and the objective, as explained later.

Eye-Pieces. — With achromatic objectives ordinary Huygenian eye-pieces are used. Two eye-pieces, respectively of 1-in. and 2-in. focal length, will generally cover the range of magnification needed.

For the taking of photomicrographs, projection eye-pieces are said to possess some superiority, especially when high-power objectives are used, as they then yield flatter and more sharply defined images. The Zeiss projection eye-piece No. 2 is very satisfactory.

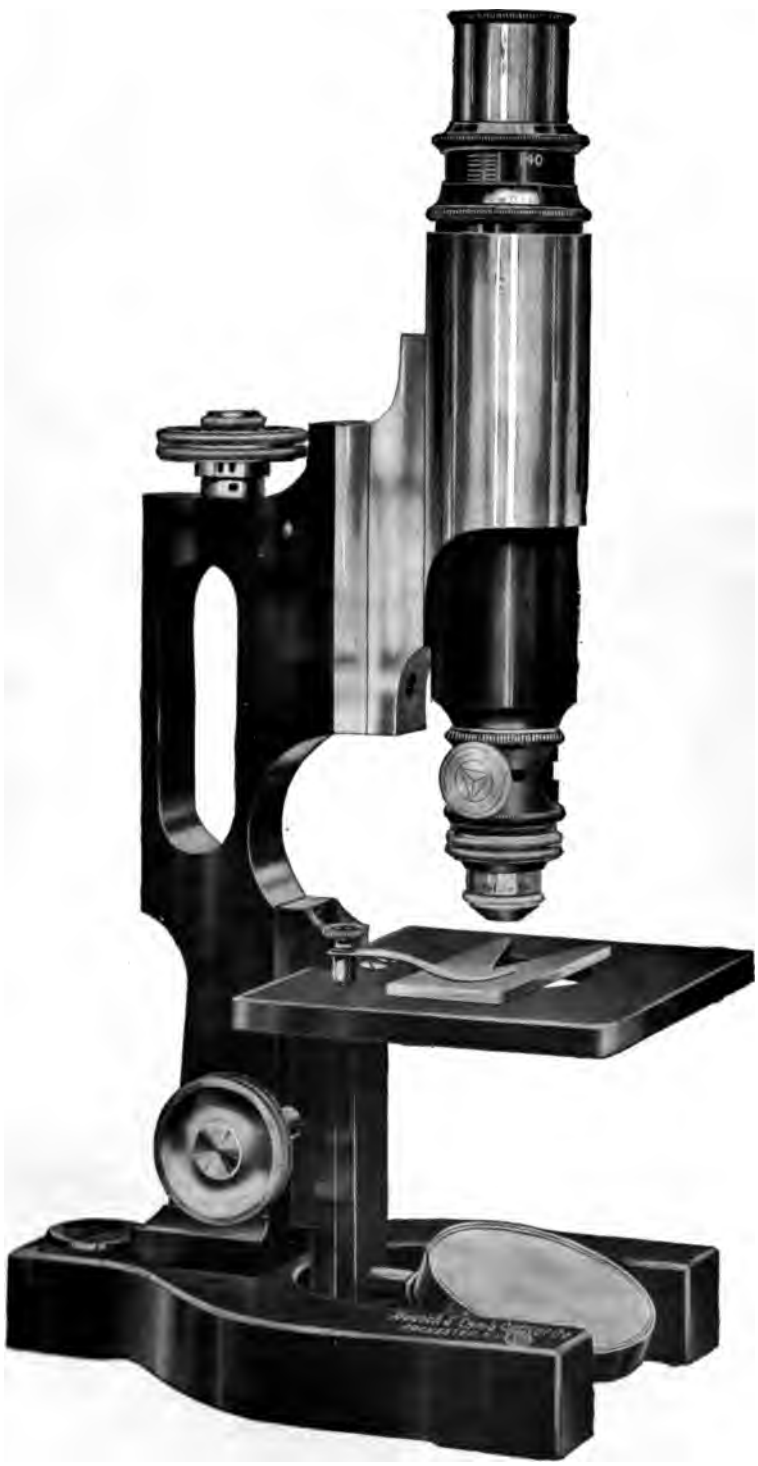


Fig. 2. — Student microscope (.6 actual size).

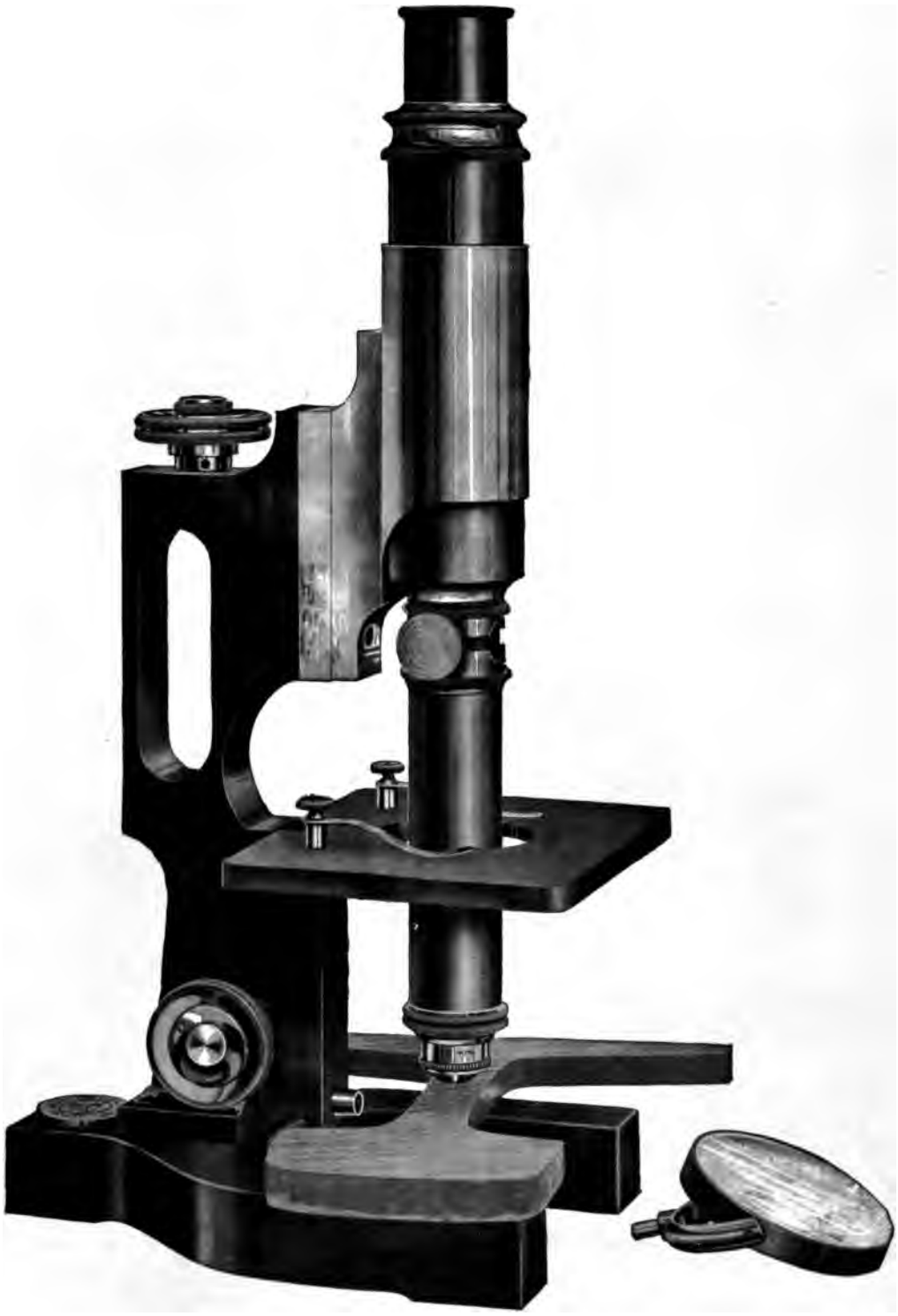


Fig. 3. — Student microscope fitted with auxiliary tube.

Fig. 2. — Student microscope (.6 actual size).

Fig. 4. — Plain revolving stage, magnetic specimen holder, and specimen.

Fig. 5. — Mechanical stage to fit metallurgical microscope, magnetic specimen holder, and specimen.

Iris Diaphragms. — Iris diaphragms are sometimes inserted between the objectives and the illuminator so as to control the size of the pencil of light proceeding from the object, with a view of securing sharper definition. Their use in that position, however, is of doubtful value, as it may cause some distortion of the image. It seems preferable to place the iris diaphragm between the source of light and the illuminator, thus regulating the amount of light *entering* the latter. When placed between the objective and the illuminator it increases, moreover, their distance apart, which we have seen to be objectionable. If a diaphragm must be attached to the microscope, it is better to place it between the tube nose and the illuminator. When using low-

32 mm. 16 mm. 4 mm.

Fig. 6. — Short mounted achromatic objectives.

power lenses it might also be screwed to the lower end of the objective, thus controlling the light returned by the object *before* entering the objective.

Specimen Holders. — In order to examine a piece of metal under the microscope, it is of course necessary that the polished and otherwise prepared surface be held in a plane accurately perpendicular to the optical axis of the instrument. This may be accomplished by so shaping the sample that it will have two sides exactly parallel, and preparing one of them for microscopical examination. This operation, however, is at best tedious and laborious, and metallographists have endeavored to replace it by the use of more or less ingenious devices for holding the specimens in the proper

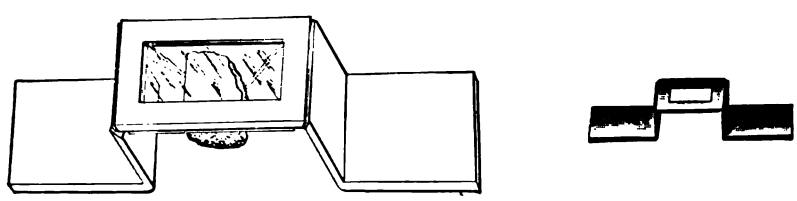


Fig. 7. — Specimen holder.

position. Some embed their samples in wax or in some other plastic material, while others have recourse to stages provided with special leveling devices.

The simple holder shown in Figure 7 gives better satisfaction, requiring no mounting whatever of the samples. The specimen, no matter how irregular in shape, is held firmly in place by a rubber band and the holder placed on the stage like an ordinary slide. If the correction of the objective demands it, a cover glass may be inserted between the sample and the holder. It will be apparent that the required manipulations are very simple and quickly performed.

In the case of specimens smaller than the opening of the holder, however, the use of a cover glass is necessary to hold them in place. This is objectionable, at least

when using high-power objectives, which should be corrected for uncovered objects. To overcome this difficulty, a little templet may be used having a triangular opening and inserted between the specimen and the holder (Fig. 8). This templet is made very thin so as to permit the use of high-power objectives, which must be brought very close indeed to the object. It will also be noticed that one side of the upper part of the holder has been removed, exposing to view a larger portion of the sample and permitting a more ready approach of high-power objectives. Large samples are, of course, placed in the holder without any templet.

A still simpler and more effective device can be used to hold in place samples of iron and steel and other magnetic substances. The device consists of a V-shaped

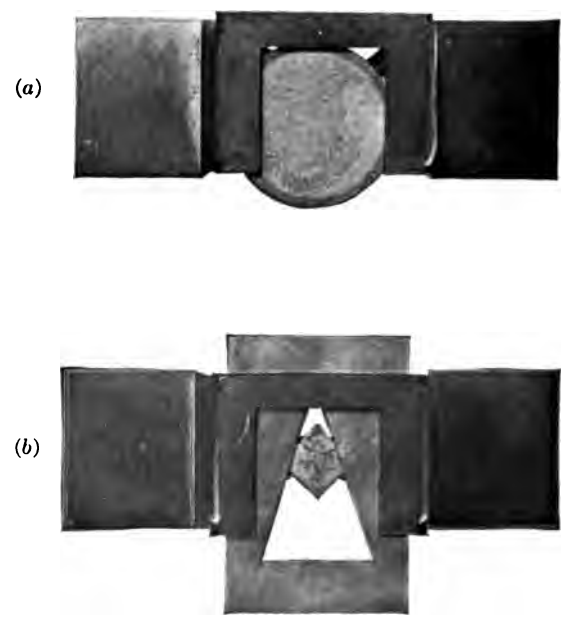
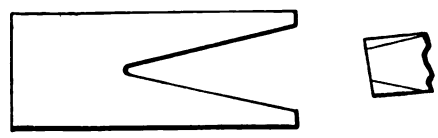


Fig. 8. — (*a*) Specimen holder and large sample.
(*b*) Specimen holder, templet, and small sample.

permanent magnet of special steel about 1 inch wide and 2½ inches long (Fig. 9). This little magnet is placed on the stage of the microscope like an ordinary glass slide (Figs. 4 and 5) and the sample to be examined suspended to it from below, being held in place by the attraction of both poles. Small samples are suspended near the small end of the V-shaped opening, while larger ones are placed nearer the wider end of the opening. This holder, therefore, is universal in its application within the limits of samples of suitable size for microscopical examination. If the opening of the stage be sufficiently large, say 1¼ inches or more in diameter, the magnet may be kept permanently on the stage, as the samples may then be readily removed or attached to the magnet with the fingers from below the stage. This adds so much to the convenience of this little device that it is strongly urged, in case the central aperture of the stage is too small, to have it suitably enlarged. The magnet is kept in place, like any glass slide, by the clips of the microscope and, also like any glass slide, may be moved about for the inspection of the different parts of the specimen. The side of the magnet

resting on the stage having been ground perfectly flat, it will be evident that the surface of the sample under examination will always be accurately in the proper position, permitting the use of high-power objectives without fear of difficulty arising from ever so slight an inclination of the sample.

When used in connection with a mechanical stage (Fig. 5) the convenience of this little holder becomes still more apparent and its usefulness is further increased. It then affords, moreover, a ready means for the repeated examination of the same spot of any sample at any time. To that effect the holder is laid upon the prepared surface and two scratches made by drawing a needle across the specimen along the sides of



(*a*) (*b*)

Fig. 9. — (*a*) Magnetic specimen holder.
(*b*) Scratched specimen.

the V-shaped opening, as shown in Figure 9. When it is desired to examine the sample, the latter is suspended to the magnet so that the needle markings coincide closely with the sides of the magnet opening, in this way securing a permanent position for the sample. The position of the magnet itself is controlled, in the usual way, by means of the graduating devices of the mechanical stage.

Finally, by placing the sample below the stage and bringing the prepared surface on a level with the stage, considerably greater working distance is secured, a gain which has its importance.

The only limitation of this holder is due to the fact that with very small speci-

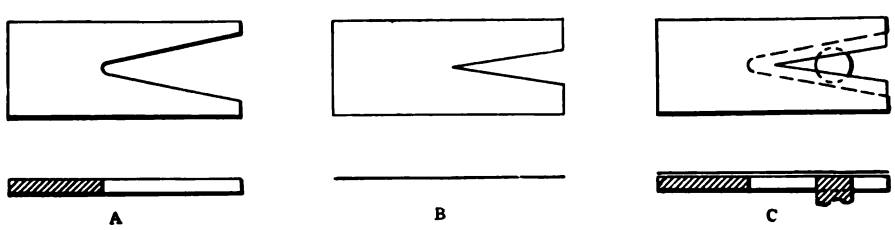


Fig. 10. — (*a*) Magnetic holder.
(*b*) Steel templet.
(*c*) Magnetic holder, templet, and sample.

mens it is impossible to use high-power objectives (1/6 inch or less in focal length), because the mounting of the objective comes in contact with the sides of the magnet and prevents the focusing of the object. For the examination by high-power objectives, the use of a very thin steel templet (not over 0.01 inch thick) of the same dimensions as the magnetic holder, but with a V-shaped opening considerably narrower (Fig. 10) is recommended. This templet is placed over the magnetic holder so as to exactly cover it, thereby becoming magnetized. The small iron and steel samples are suspended to this thin steel plate in the usual way and may then be examined with the highest power objectives.

Universal Metalloscope. — The instrument shown in Figures 11 to 15 was devised especially for the ready examination of large iron and steel samples, but it will be apparent that it can be used with equally satisfactory results for small samples both opaque and transparent.

The microsope stand proper consists of a microscope-tube, provided with both coarse and fine adjustments, and with a draw-tube, rigidly mounted on a bar supported at both ends on substantial and firm cast-iron legs.[1] The height between the table and the under side of the supporting bar is 5 inches and the distance between the supporting legs 12 inches.

This arrangement affords free space below the objective for the examination of

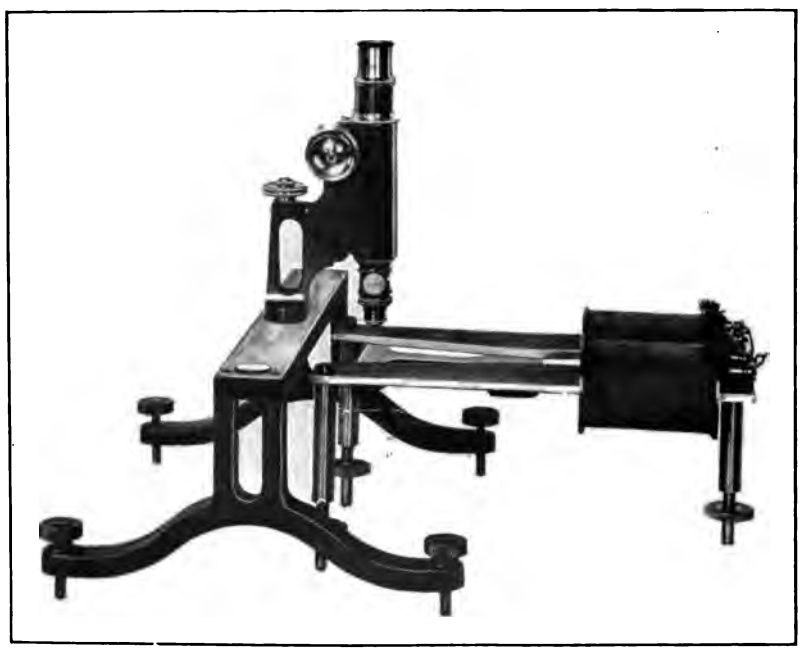


Fig. 11. – Universal metalloscope: stand, eye-piece, vertical illuminator, objective, electromagnetic stage, and rail section.

large specimens of metals, such as full rail sections, without detracting in the least from the value of the instrument when applied to the examination of the usual small specimen, as explained later. Many metal microscopists frequently have to examine bulky specimens, and this is altogether impossible with the ordinary microscopes as well as with the special metallurgical microscopes which have been designed and described from time to time.

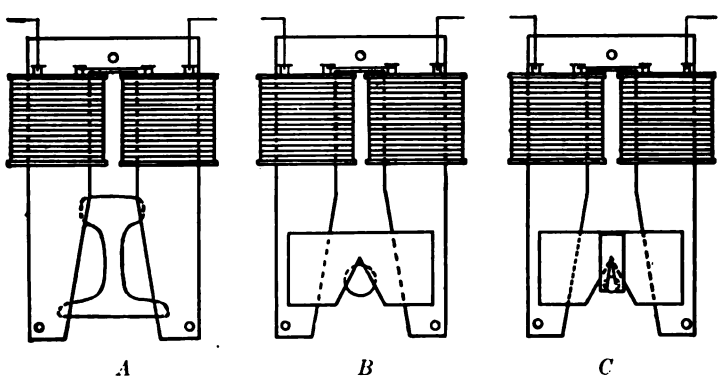
Recourse must be had to all sorts of makeshifts for the proper support of large specimens, or, more often, the microscopist gives up the attempt altogether, or else resigns himself to the cutting of the bulky samples into small pieces to be laboriously polished and separately examined.

It is believed that an instrument permitting the examination of large as well as

[1] In a more recent model the supporting bar is mounted on *three* legs, permitting the ready leveling of the instrument.

of small specimens with equal ease and accuracy will be welcomed by metallographists, and that it will lead to more frequent examinations of full sections of metal implements, a departure which should bring fruitful results.

Electromagnetic Stage. — The perplexing question of the proper support, for microscopical examination, of iron and steel specimens of all sizes and shapes has been effectively solved by the use of the electromagnetic stage illustrated in Figure 11. This stage consists of a steel plate 7 by 14 inches having a V-shaped opening, and converted into a powerful electromagnet by means of two bobbins with solenoids surrounding the arms of the steel plate, as clearly shown in the illustration. Electrical connection is readily made with any suitable current, and the use of an incandescent lamp in series provides in a simple way the necessary outside resistance to prevent heating of the solenoids. Large specimens of iron and steel, such as rail sections, *A*, Figure 12, are firmly held in an accurate position by the attraction of the magnetic stage, the extremities of the flange only and a narrow space on each side of the



A *B* *C*

Fig. 12. — (*A*) Electromagnetic stage and rail section. (*B*) Electromagnetic stage, templet, and medium-size specimen. (*C*) Electromagnetic stage, two templets, and small specimen.

head being hidden from view. The size and shape of the stage-opening make possible the ready support of specimens measuring from 2 to 6 inches in their greatest dimension.

Templets for the Examination of Small Specimens. — For the examination of iron and steel samples from 2 inches in length down to the smallest dimensions, a steel templet, also with a V-shaped opening, is placed on the stage, shown at *B*, Figure 12. This templet through its contact with the stage becomes strongly magnetized and the specimens to be examined are suspended to it.

For the examination of very small specimens with high-power lenses the thickness of this templet would prevent the necessary close approach of the objective. To make this approach possible a very thin steel templet (not exceeding 0.01 inch thick) is used, shown at *C*, Figure 12, which makes possible actual contact between a high-power objective and the smallest specimen.

Support of Non-Magnetic Specimens. — For the support of non-magnetic specimens, such as non-ferrous metals, rocks, cement, etc., a very simple device is provided, consisting of two crossbars and rubber bands, which is readily attached to the stage and by means of which the non-magnetic specimens, as well as the templets when needed, are firmly held in place regardless of their size or shape.

Leveling-Devices of Stand and Stage. — It is, of course, essential, especially when using high-power objectives, that the optical axis of the microscope be accurately perpendicular to the surface under examination. To secure this result both the stand and the stage are provided with leveling-screws, as shown in Figure 11. For leveling the stage a small spirit-level may be placed upon it, or better, upon the sample under examination, and the necessary adjustment quickly made. For leveling the microscope stand the eye-piece should be removed, the small level placed on top of the tube, and the leveling-screws adjusted. By placing the instruments on a table or desk having a smooth and flat top, it is evident that, barring accidents, the stand and stage will remain indefinitely accurately leveled.

Motion of the Stage. — In order to examine the entire surface of a large specimen it is necessary to bring in turn within the field of the microscope the different portions

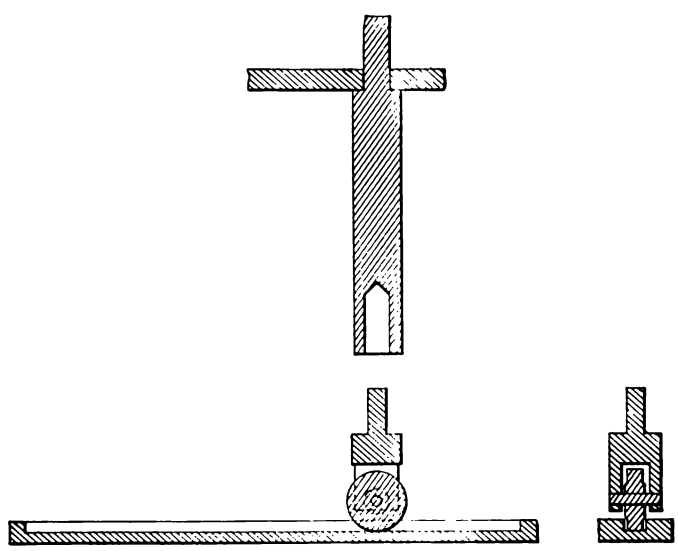


Fig. 13. — Back leg of electromagnetic stage and sliding plate.

of the specimen, and this necessitates the moving of the stage in various directions. The weight of the stage, however, would create considerable friction between the legs and the supporting table, making the sliding motion jerky and otherwise unsteady. To overcome this difficulty the back leg of the stage is provided with a small wheel running in a groove cut in a small brass plate fastened to the table or desk, shown in Figure 13. The mounting of the wheel is provided with a pivot fitting snugly into a hole in the leg. This construction makes possible the ready back-and-forth motion of the stage, as well as its free circular displacement around the axis of the back leg thus permitting to bring quickly any desired portion of the object under the objective. As the bulk of the weight is supported by the back leg, the arrangement makes possible a very steady and smooth motion of the stage.

Mechanical Stage. — The use of a mechanical stage is often highly desirable. This [illegible] in the present instrument in two different ways: (1) by the use of a [illegible] suitably attached to the electromagnetic stage, and (2) by the use [illegible] independently mounted on a separate base of the usual horseshoe [illegible]

The first method is illustrated in Figure 14. A mechanical stage of usual construction is screwed on a brass plate provided with two small pins fitting two corresponding holes in the magnetic stage, thus securing a firm and constant position for the mechanical stage. When using a mechanical stage, however, a rigid and constant position should also be secured between it and the microscope stand. To that effect a brass plate is provided, with recesses to receive the back legs of the stand as well as the front legs of the stage, shown in Figure 14. It is then possible at any time to place the microscope stand and the stage in exactly the same relative positions.

The second method consists in the use of a mechanical stage separately mounted on an ordinary horseshoe base, shown in Figure 15. To secure a constant relative

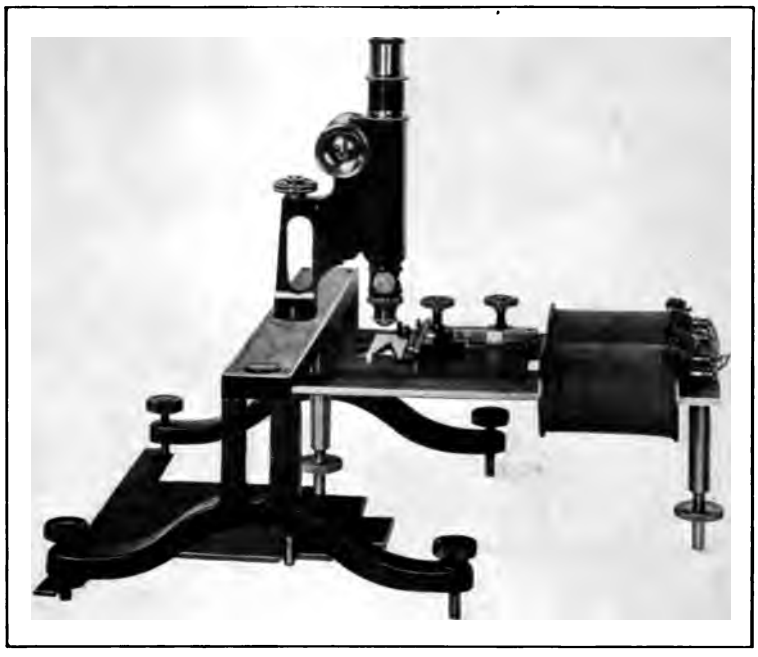


Fig. 14. — Universal metalloscope: electromagnetic stage with mechanical stage, magnetic specimen holder, small specimen, and base-plate.

position between stand and stage, the foot of the latter fits into recesses provided for that purpose in the base-plate.

The use of this independently mounted mechanical stage offers the additional advantage resulting from the vertical up-and-down racking of the stage, rendering unnecessary any vertical adjustment of the light and condenser, as well understood by metallographists.

Examination of Transparent Objects. — To adapt the universal metalloscope to the examination of transparent objects, thereby converting it into an ordinary microscope, or, if desired, into a petrographical microscope, a separate stage on horseshoe base should be used, as shown in Figure 15, when the necessary Abbe condenser, analyzer, polarizer, etc., can readily be attached. The instrument is then in no way inferior to high-class microscopes for examination by transmitted or polarized light.

ILLUMINATION OF THE SAMPLES

Opaque objects such as metals and alloys must necessarily be examined by reflected light, i.e. by light thrown upon them from above the stage, their treatment differing in this respect from that of other microscopic preparations, which are generally examined by transmitted light, i.e. by light sent through them and proceeding from below the stage.

With the low-power objectives there are two possible ways of illuminating opaque specimens: (1) by directing the light obliquely upon the object, and (2) by causing the light to fall perpendicularly upon it by means of so-called "vertical illuminators."

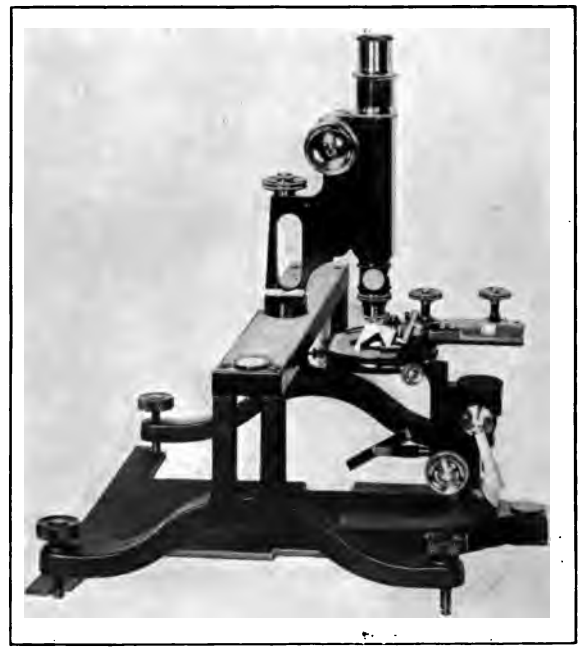


Fig. 15. — Universal metalloscope: mechanical stage on horseshoe base, magnetic specimen holder, small specimen, and base plate.

With medium-high and high-power objectives the second method only is possible, because the distance between the specimen and the front lens of the objective is now so small that obliquely reflected light cannot reach the surface under examination. With very low-power objectives — i.e. having a focal length of one inch or more — the vertical illuminator may be placed between the lens and the object; but with higher power objectives it must of course be inserted between the objective and the microscope tube, the objective then acting as a light condenser and increasing the intensity of the illumination.

Oblique illumination may be obtained (*a*) by allowing daylight or artificial light to fall freely upon the object; (*b*) by directing the light upon the object by means of mirrors, reflectors, or condensers; (*c*) by the use of a "lieberkühn"; and (*d*) by the use of a "parabolic reflector."

Vertical illumination may be produced (*a*) by means of an opaque reflector consisting of a totally reflecting prism or of a mirror covering only a portion of the objective, the light returned by the object reaching the eye by passing through the uncovered portion; and (*b*) by means of a transparent reflector, generally a plain glass disk or glass square, reflecting upon the object a portion of the incident light and permitting the passage of a portion of the light returned by the object, which thus reaches the eye.

When a highly polished surface is examined by obliquely reflected light, since the angle of reflection is equal to the angle of incidence, the totality of the light is reflected outside the objective (Fig. 16) and the object appears uniformly dark. In case the metallic specimen contains some portions duller in appearance, these will scatter a certain amount of light a part of which will enter the objective (Fig. 16), and those portions will therefore appear brighter. A similar effect is produced when the speci-

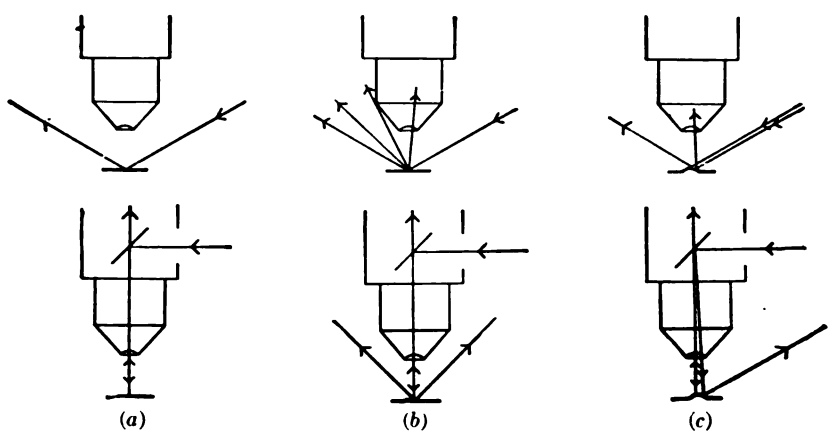


Fig. 16. — (*a*) Oblique and vertical illuminations of bright surface.
(*b*) Oblique and vertical illuminations of dull surface.
(*c*) Oblique and vertical illuminations of hills and valleys.

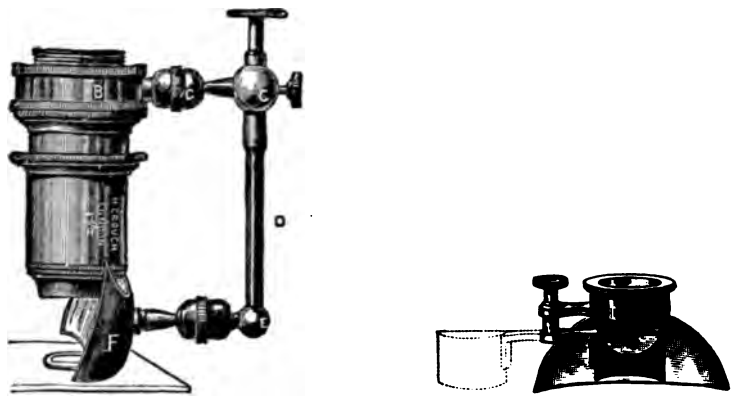
men, instead of being perfectly flat, contains microscopic hills and valleys, the sides of which may be so inclined as to reflect some light into the microscope (Fig. 16), consequently appearing bright. Viewed by oblique light, therefore, the relative darkness or brightness of a constituent will vary inversely with its true appearance and will also depend upon its orientation, since this will affect the angle of incidence of the light striking it. Generally speaking, the darker a constituent the brighter will it seem to be when illuminated by oblique light, the latter yielding, so to speak, a negative image. Oblique illumination, moreover, cannot be made as intense as vertical illumination and, as already explained, is possible only with low-power objectives. For these and other reasons, while it is not without value, it is only used occasionally by metallographists.

To increase the intensity of oblique illumination and to make its use possible with somewhat higher powers, such appliances as the "lieberkühn" and the parabolic reflector have been used. The "lieberkühn," so called from the name of its inventor, consists of a small concave mirror attached to the objective and reflecting upon the object some light proceeding from below the stage and passing around the object. It will be evident that only small size objects can be thus illuminated.

The parabolic reflector (Fig. 17), first constructed by Messrs. Beck of London for Dr. Sorby, consists of a parabolic mirror placed on one side between the objective and the object and condensing the incident light upon the latter. It should be attached to the objective. Dr. Sorby later added a silver mirror in the shape of a half disk to the same mount, so as to be able to obtain at will vertical and oblique illumination when using low-power objectives (Fig. 17). When vertical illumination is desired, the small mirror is swung over the objective, covering only a portion of it, and directing vertical rays of light upon the object. This combination is known as the Sorby-Beck reflector.

The effects of a vertical illumination are precisely opposite to those of an oblique illumination, as clearly shown in Figure 16, highly polished surfaces reflecting the totality of the light into the objective, while dull ones appear dull because they reflect most of the light outside.

To produce a vertical illumination we have the choice between an opaque or a



(*a*) (*b*)

Fig. 17. — (*a*) Parabolic reflector.
(*b*) Sorby-Beck parabolic reflector.

transparent (glass) reflector. The opaque reflector consists of a totally reflecting right-angled prism, or of a mirror placed between the microscope tube and the objective and covering only a portion (generally about one half) of its aperture. The beam of light enters the illuminator through a side opening provided for that purpose and is reflected downwards by the reflector, being condensed upon the object by the lenses of the objective itself. The light sent back by the object reaches the eye through the uncovered part of the objective.

The first vertical illuminator was designed by Professor Hamilton L. Smith of Hobart College, Geneva, N. Y., and consisted of a small annular silver mirror (Fig. 18), forming an angle of 45° with the axis of the microscope, the light reflected by the object passing through the central opening on its way to the eye. Semi-circular mirrors, similarly mounted and partially covering the objective (Fig. 18), have been used with equal satisfaction, and the author has obtained good results with a very small central mirror (Fig. 18) suitably mounted, reflecting the light upon the central portion of the objective lenses, and permitting the returned light to reach the eye through the free space surrounding the mirror.

Instead of a mirror, a totally reflecting right-angled prism may be used as shown

in Figures 18 and 19, covering half of the aperture of the objective. The prism is so mounted that it can be rotated around its horizontal axis, this being needed in order to secure the best illumination of the sample. Nachet, of Paris, provides his prism with an additional motion permitting it to cover a greater or smaller portion of the objective. These reflecting prisms are now used much more than the reflecting mirrors.

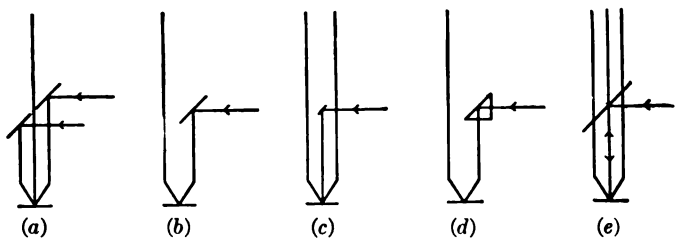


Fig. 18. — (*a*) Annular mirror.
(*b*) Semi-circular mirror.
(*c*) Central mirror.
(*d*) Totally reflecting prism.
(*e*) Plain glass disk.

In 1874 Nachet constructed for the International Commission of the Meter some objectives provided with totally reflecting prisms as permanent parts of their mountings. In low-power objectives a prism was placed above the first lens (Fig. 20), while with higher power objectives it was necessarily inserted above the double or triple lens system. These objectives are called illuminating objectives. This arrangement,

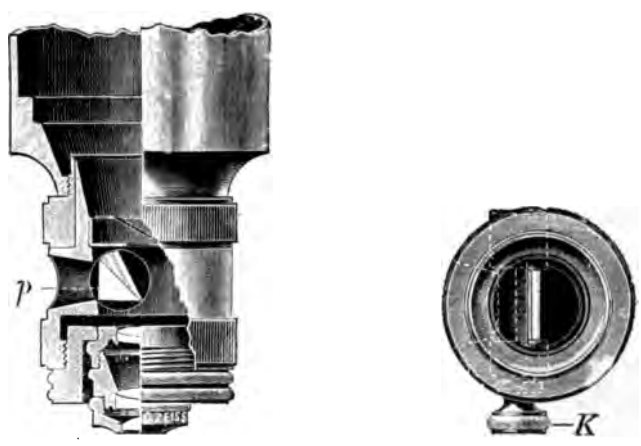


Fig. 19. — Vertical illuminator. Totally reflecting prism. Zeiss.

however, has not been found very satisfactory and with one notable exception is seldom used by metallographists.

In vertical illuminators having a transparent reflector, the latter consists of a plain glass disk covering the whole of the aperture of the objective (Figs. 18 and 21). The incident light is in part reflected upon the object, while another portion passes freely through the glass reflector. A part of the light returned by the object is again reflected by the glass illuminator, while another portion passes through it and thus reaches

the eye. The glass reflector is so mounted that it can be rotated around its horizontal axis (Fig. 21). The amount of light permitted to enter the illuminator may be regulated by an iris diaphragm attached to the side opening or independently mounted and placed between it and the source of light, or by a revolving sleeve attached to the illuminator and provided with different size openings. The first plain glass illuminator was constructed by Mr. Beck of London.

With very low-power objectives it is preferable to place the vertical illuminator

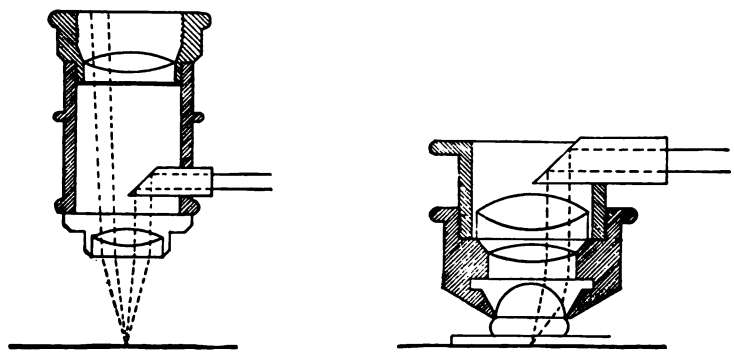


Fig. 20. — Nachet illuminating objectives.

between the objective and the object, attaching it to the former in some suitable way, as for instance by providing the lower end of the objective with a society screw (see Fig. 6).

While the author is well aware that some metallographists of note prefer the prism to the plain glass type of vertical illuminator, in his opinion the plain glass reflector is greatly superior. While the illumination obtained by its use is not quite as intense, it is certainly more uniform and less liable to produce a distortion of the image.

An improved construction of the plain glass vertical illuminator is illustrated in

Fig. 21. — Bausch and Lomb plain glass disk vertical illuminator.

Figure 21. The glass reflector is inserted into a brass ring which on the side opposite the milled head is screwed into the wall of the brass mounting, practically doing away with the frequent breaking of the glass and greatly facilitating its cleaning. The milled head is large, which makes it possible to impart a more delicate motion to the glass reflector.

SOURCES OF LIGHT AND CONDENSERS

The illumination of opaque objects such as metals and alloys requires an intense source of light, especially for their photography. Daylight and ordinary gas or oil flame should be discarded as not suitable for the purpose, the sources of light which

have been found most satisfactory being, in the order of their excellence, intensity, and decreasing cost: (1) the electric arc lamp, (2) the Nernst lamp, and (3) the Welsbach gas lamp.

The Welsbach lamp outfits (Figs. 22 and 23) are very inexpensive and quite satis-

Fig. 22. — Welsbach lamp and double-convex condensing lens.

factory for visual examination by low- and medium high-power objectives. In taking photomicrographs, however, their lack of intensity necessitates very long exposures, while with high-power objectives the light received upon the camera screen

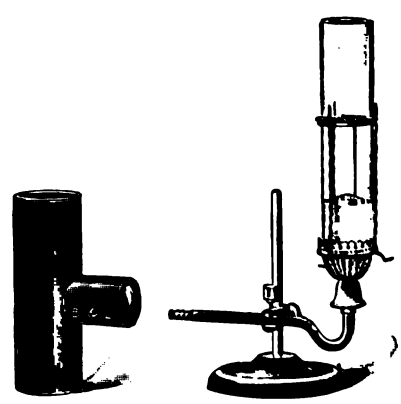


Fig. 23. — Welsbach lamp and bull's eye condenser.

is so faint as to render proper focusing of the object a very difficult, if not impossible, operation.

Two kinds of electric arc lamps are now supplied, one with large carbons (Fig. 24) and a smaller one with carbons measuring only ¼ inch in diameter (Fig. 27). The carbons should be placed at right angles, as this arrangement directs the maximum amount of light into the condensers. The positive or horizontal carbon should be cored and larger than the vertical or negative carbon. While automatic feeding of

the carbons (Fig. 26) is a valuable feature, it is not by any means essential, as remarkably effective hand-feed lamps are now constructed by which a very steady light can be maintained (Fig. 25). Automatic mechanisms, moreover, are liable to get out of order and occasional sudden shiftings of the light are difficult to entirely eliminate.

The large carbon lamp yields, of course, by far the most intense illumination and

Fig. 24. — Large arc lamp outfit.

is the only one suitable for direct projection of metallic samples upon a screen for public exhibition. In taking photomicrographs with the large arc lamp the needed exposures are often instantaneous and seldom exceed five or, at the most, ten seconds. The lamp consumes from fifteen to twenty amperes.

The small arc lamp (Fig. 27) is very satisfactory for visual examination and is, of course, much less expensive. It, however, requires longer exposures when photo-

Fig. 25. — Hand-feed arc lamp.

Fig. 26. — Automatic feed arc lamp.

graphing. The position of the carbons can be regulated with great nicety by independent adjustments, thus securing a very uniform light. The lamp consumes about five amperes.

The Nernst lamp (Fig. 28) is used successfully by many microscopists and undoubtedly affords a very satisfactory illumination both for visual examination and for photomicrography. In taking photographs, exposures of ten seconds or more are needed, according to the magnification and the character of the specimen.

Summing up, if we desire a cheap and convenient form of illumination for visual examination with objectives of low and medium high power, the Welsbach lamp will be found in every way satisfactory; while for the taking of photomicrographs and for examination by high-power objectives the electric arc lamp and the Nernst lamp should be recommended, bearing in mind that the large arc lamp will yield light of

Fig. 27. — Small electric arc lamp, bull's eye condenser, and rheostat.

greatest intensity but will, on the other hand, be much more costly. When neither gas nor suitable electric current are available, an acetylene lamp should be used, provided tanks of acetylene gas can readily be obtained.

Condensers. — Some kind of condensing attachment must be placed between the source of light and the vertical illuminator so that a large portion of the light may be utilized and a beam of suitable size directed into the illuminator. In the case of light

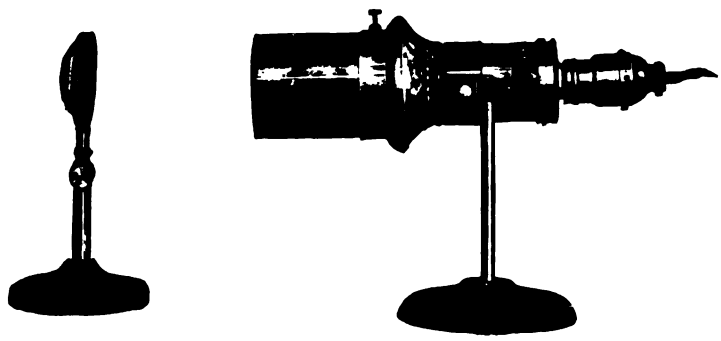


Fig. 28. — Nernst lamp and special bull's eye condenser on adjustable supports.

proceeding from a luminous point or at least from a small luminous area, as for instance with the electric arc, at least two lenses or systems of lenses are needed, one system, PL and ML (Fig. 29), placed near the source of light, to collect the divergent rays and convert them into a parallel beam, and a second lens CL placed at some distance from the first, to convert the parallel beam into a converging one. The vertical illuminator should be located at such a distance from the condensing lens that the beam

of light will cover a little more than the opening through which it enters the illuminator. A glass cooling cell *CC*, filled with distilled water or some other suitable liquid, should be placed between the two lenses in order to absorb a large amount of heat and thereby prevent injury to the objective. An iris diaphragm, *I*, should also be used to control the amount of light entering the vertical illuminator. This diaphragm should be placed in front of the converging lens and should be provided with clips for holding ground and colored glasses. These various parts should be mounted on a so-called "optical bench" *B* upon which they can slide.

With a large luminous body such as the Welsbach mantle, a single double-convex lens (Fig. 22) or a bull's eye condenser (planoconvex) (Fig. 23) is sufficient to collect and condense the necessary amount of light. It should, of course, be placed at the proper distance both from the vertical illuminator and from the source of light. The use of an iris diaphragm attached to the lens or on a separate mount is advisable, since it affords a ready means of controlling the amount of light admitted into the illuminator.

Monochromatic Light. — The different lamps described above all yield, of course,

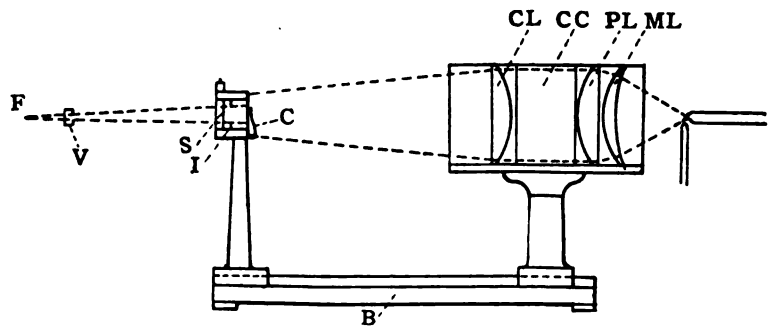


Fig. 29. — Condensing lenses, cooling cell, iris diaphragm, automatic shutter, and optical bench.

white light, and since the correction even of apochromatic objectives for chromatic aberration is never perfect, it is evident that the use of monochromatic light — i.e. light of one wave length — is preferable, especially for photographing. Monochromatic light may be obtained in two ways: (*a*) by using a source of light actually monochromatic, and (*b*) by causing white light to pass through colored glass screens or colored solutions (light filters), preventing the passage of some undesirable rays. The mercury arc lamp yields a nearly monochromatic light and has been tried by Le Chatelier with satisfactory results. It seems more convenient, however, when monochromatic light is wanted, to use light filters of suitable colors, in which case colored glass screens will be found easier to manipulate than glass cells containing colored solutions.

PHOTOMICROGRAPHIC CAMERAS

For taking photomicrographs, a light-tight connection should be established between the microscope and camera, both instruments being placed vertically or horizontally (Figs. 30 and 31). Whether to use the camera in a vertical or horizontal position is a debatable and debated question. Among well-known metallographists, Le Chatelier and Martens prefer the horizontal while Osmond and Stead have a strong

Fig. 30. — Photomicrographic camera (vertical position), showing metallurgical microscope, mechanical stage, automatic shutter, etc.

Fig. 31. — Photomicrographic camera (horizontal position) showing metallurgical microscope (horizontal position), mechanical stage, automatic shutter, etc.

Fig. 32. — Metallurgical microscope (vertical position) connected to camera (horizontal position) by means of totally reflecting prism; showing automatic shutter, large arc lamp outfit and thread belt for manipulating microscope fine adjustment.

preference for the vertical position. The latter certainly affords greater stability and eliminates all danger of heavy specimens slipping while being photographed. It is often said that the vertical position is inconvenient because of the necessity of mounting on a stool for focusing the image on the screen, but the objection appears trifling. It is also argued by some that the microscope should be used in a horizontal position because this makes it possible for the operator to sit while performing his work. This objection also appears to have little weight.

By the use of a large, totally reflecting prism, however, connecting the microscope

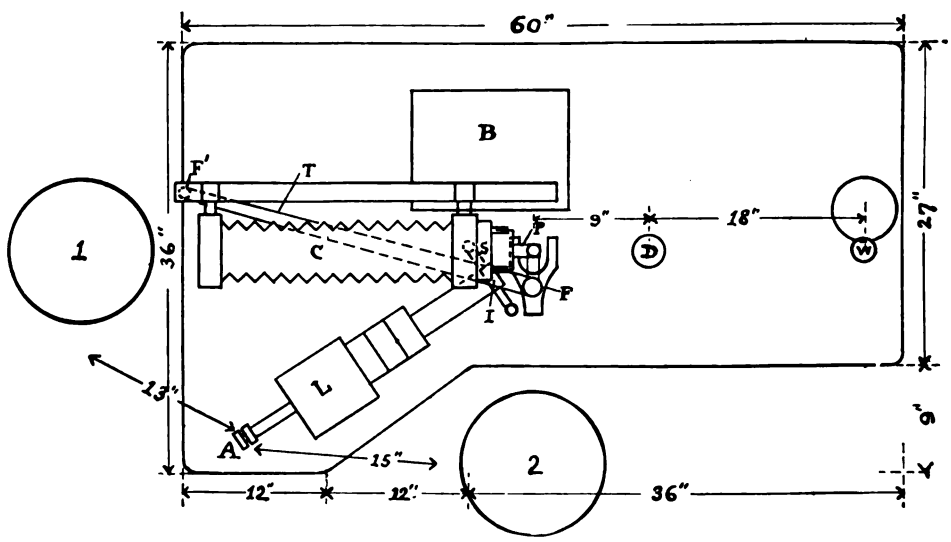


Fig. 33. — Plan view of metallurgical microscope and photomicrographic camera joined by totally reflecting prism; large arc lamp outfit and Welsbach outfit No. 5.

Legend: C = camera.
B = camera base in reversed position.
F = Fine adjustment of microscope.
F' = Pulley for controlling F from the position, 1, of the observer at the camera.
L = Arc lamp outfit.
I = Iris diaphragm.
P = Horizontal vertical attachment.
S = Automatic shutter with iris diaphragm.
W = Welsbach lamp arranged for visual examination at same microscope.
D = Condenser for Welsbach lamp.
2 = Position of observer at microscope.
A = Adjustment for arc lamp carbons.

and camera (Figs. 32 and 33), it is possible to maintain the microscope vertical, undoubtedly the best position, while using the camera horizontally. A thread belt connects the fine adjustment of the microscope with a pulley mounted on a standard at the end of the camera bed bar. This enables the operator to control the fine adjustment easily from his position at the camera screen, while the placing of the arc lamp on the same side of the microscope as the camera makes it possible for him to reach with his right hand the various adjustments of the lamp, thus securing maximum intensity and uniformity of illumination, two points so essential in taking photomicrographs.

For visual examination, the front standard of the camera to which the special prism

Fig. 34. — Universal metalloscope, Nernst lamp outfit, and vertical camera.

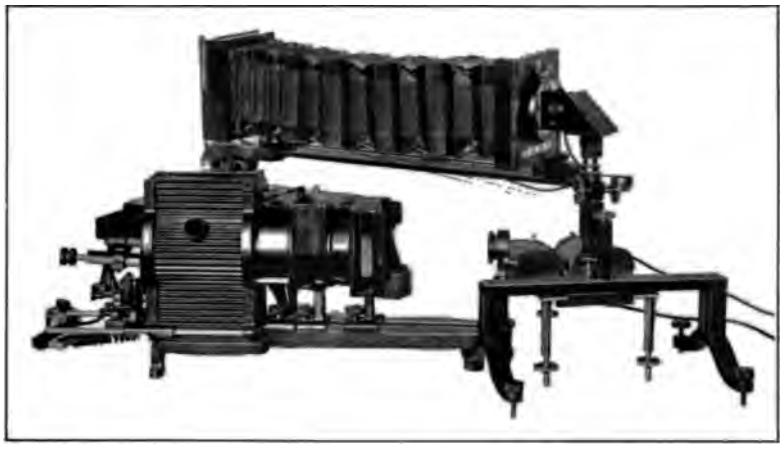


Fig. 35. — Universal metalloscope, arc lamp outfit, large totally reflecting prism, and horizontal camera.

is attached is moved along the bed bar to a sufficient distance. To bring the camera into position for photography the front standard is brought towards the microscope until the collar beneath the prism rests upon the eye-piece of the microscope, the focus of the microscope not being changed in the least. The bottom of this collar which is fitted with a felt rim rests directly upon the eye-piece without exerting any pressure, but tightly enough to make a light-tight connection. The image is then focused upon the camera screen by the fine adjustment alone and the exposure quickly made.

The universal metalloscope already described is seen in Figure 34 with vertical camera and Nernst lamp and in Figure 35 with horizontal camera, totally reflecting prism and large arc lamp.

INVERTED MICROSCOPES

Le Chatelier was the first to suggest the use of an inverted microscope for the examination of metallic surfaces (see Appendix). In this style of microsope the stage is placed horizontally *above* the objective, the latter being necessarily pointed upwards (Figs. 36 to 38).

In the inverted type of microscope and photographic attachment illustrated in these pages, it has been attempted to simplify the construction with corresponding material decrease in price.

The microscope is *permanently* connected with the camera by a totally reflecting prism P (Fig. 37) set rigidly below the vertical illuminator. A separate tube set at right angles to the first is provided for visual examination, another totally reflecting prism P' (Figs. 37 and 38) being fastened to the inner end and serving to reflect the image from the body tube through the eye-tube to the eye. When a photograph is to be taken this prism P' is simply withdrawn from the field by means of the draw tube. The eye-tube is fitted with pin and slot which mark the limits to which the small prism P' may be pushed in and withdrawn, so that the vertical illuminator being once set, the only adjustment necessary is at the arc lamp. With the Nernst and Welsbach lamps, after the light and the vertical illuminator are once set, no more adjustments are necessary. The two totally reflecting prisms need never be rotated and in fact cannot be moved, except for the sliding motion of the prism P' as already described.

The stage, which is revolving and provided with centering screws, is of course equipped with both coarse and fine adjustment, and a mechanical stage may readily be substituted for the plain stage.

With this inverted microscope the use of a magnetic holder will also be found very convenient, for the sample is then held firmly in place instead of resting loosely on the stage, thereby increasing the usefulness of the mechanical stage.

The placing of the light on the same side of the microscope as the camera makes it possible for the operator to regulate his illumination while focusing the object on the camera's screen.

POLISHING APPARATUS

Hand Polishing. — When, in spite of the length and laboriousness of the operation, iron and steel samples are to be polished by hand, four smooth blocks of wood should be prepared, some 6 by 10 inches and 1 inch thick. One of these should be covered with canvas or linen duck and the others with fine broadcloth. The blocks are to be used as described in Lesson III, page 5.

Fig. 36. — Inverted microscope, camera, mechanical stage, and large arc lamp outfit.

Polishing by Power. — The power polishing machine shown in Figure 39 has been found very satisfactory. It consists of a heavy iron pedestal upon which is mounted a grinder having emery-wheel and cast-iron disks revolving in a vertical plane, thus giving four polishing surfaces of graduated fineness. The polishing powders mixed with water are applied to the various disks by means of brushes, and shields are provided to catch any surplus water that may be thrown off during the operation. Should a cloth become worn or torn it is readily and quickly replaced. This machine very much shortens the time necessary for the preparation of samples and is far superior to those where only one block is made to rotate at a time. A speed of 1200 revolutions per minute has been found most satisfactory for polishing iron and steel samples, but

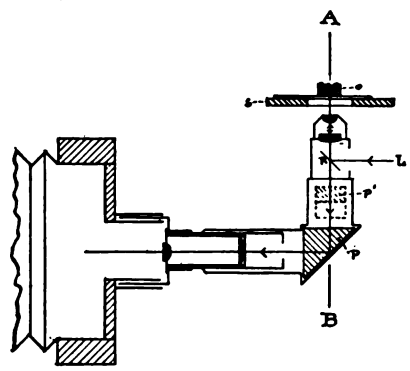


Fig. 37.

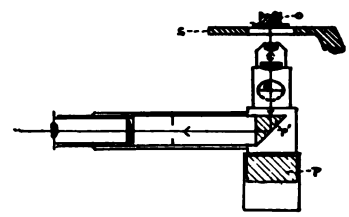


Fig. 38.

Fig. 37. — Inverted metalloscope. Vertical section, front view.
Fig. 38. — Inverted metalloscope. Vertical section, end view on AB (Fig. 37).

L = Source of Light.
R = Vertical illuminator reflector.[1]
P′ = Totally reflecting prism which reflects image into the eye-tube when latter is pushed in.
P = Totally reflecting prism which reflects image into camera when eye-tube is pulled out.
S = Metalloscope stage.
O = Specimen.

by the use of a variable speed electric motor to run the polishing machine various speeds may be readily obtained.

The polishing motor shown in Figure 40 possesses the advantages of directly driven over belt driven machinery. It is provided with the same polishing disks as the polishing machine and can be built both for constant and for variable speed.

The operation of polishing with these machines is described in Lesson III, page 6.

PYROMETERS AND ELECTRIC FURNACES

Pyrometers. — The Le Chatelier thermo-electric pyrometer is undoubtedly the instrument best adapted to the measurement of temperatures needed to control such heat treatments as are likely to be performed in a metallographical laboratory. The thermo-couple consists of a wire of pure platinum and of a wire of platinum alloyed with 10 per cent of rhodium or iridium. To measure the electromotive force created

[1] A reflecting prism may of course be used if preferred.

Fig. 39. — Power polishing machine.

Fig. 40. — Polishing motor.

by heating the couple the author does not know of any more accurate and reliable instrument than the galvanometer constructed by Siemens and Halske (Fig. 41).

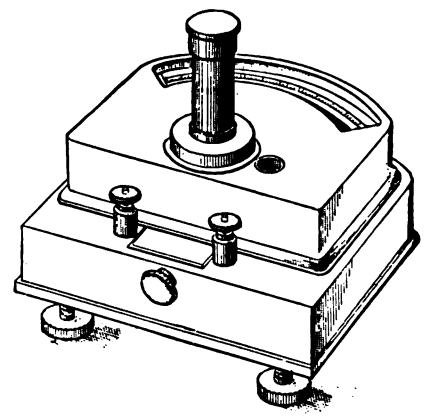


Fig. 41. — Siemens and Halske galvanometer.

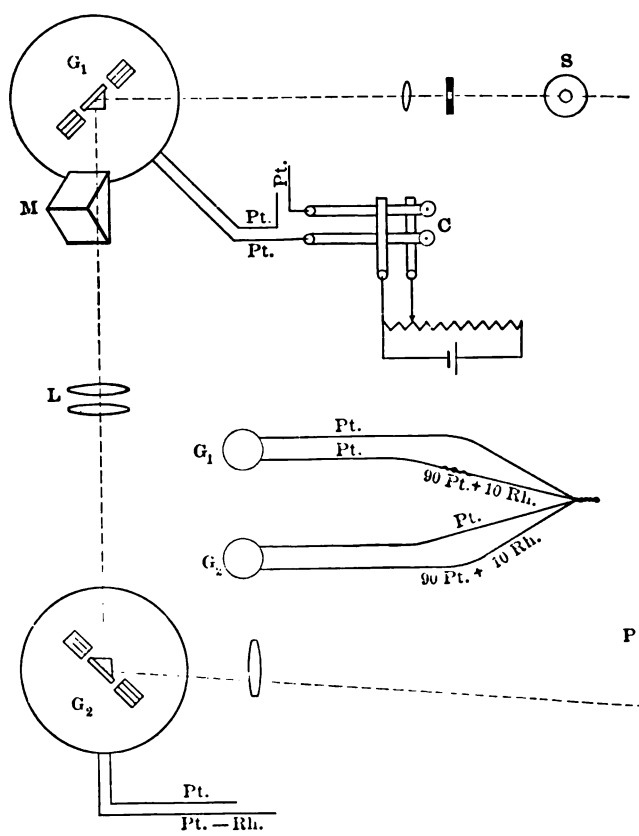


Fig. 42. — Saladin self-recording thermo-electric pyrometer.

In its latest form it has a resistence of 400 ohms, has a scale of 180 divisions, each one corresponding to 10 microvolts and a second graduation giving the temperature

directly for the couple sold with the apparatus. The use of cheaper couples and cheaper galvanometers is not to be commended for they are unsuitable for accurate scientific work and uncertain even for controlling industrial operations.

An autographic recording pyrometer is very useful and quite indispensable for the detection of faint evolutions or absorptions of heat. Indeed without its use there

Fig. 43. — Le Chatelier-Saladin self-recording thermo-electric pyrometer.

Fig. 44. — Le Chatelier-Saladin self-recording thermo-electric pyrometer.

are many delicate thermal treatments that could not be performed. Several autographic instruments are now constructed. To meet the needs of the metallographist the author believes that the pyrometric recorder designed by Le Chatelier and Saladin and constructed by Pellin of Paris (Figs 42 to 45) will be found most satisfactory. In an early form the different parts were arranged as shown in Figure 42. The light proceeding from the source S after passing through a lens is received by the mirror of a sensitive galvanometer G_1 the deflections of which measure the difference in

temperature between the sample under examination and the neutral body. This horizontal deflection of the beam of light is converted into a vertical deflection by passing through a totally reflecting prism M placed at an angle of 45 deg.

This vertically moving beam of light is received by the mirror of a second galvanometer G_2 whose deflections are a measure of the temperature of the sample. The

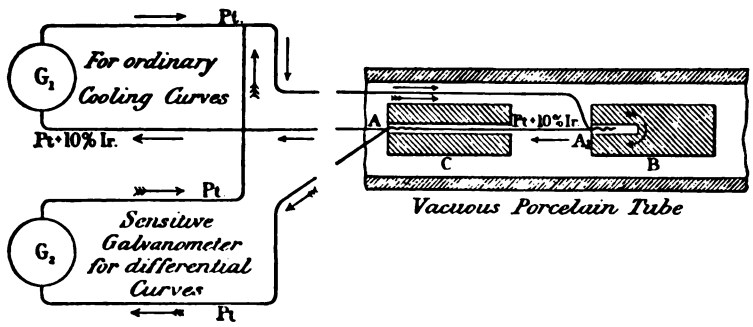


Fig. 45. — Roberts-Austen method of connecting the sample, neutral body, and galvanometers.

Fig. 46. — Heraeus electric muffle furnace.

beam then passes through a lens and reaches the screen or plate P. L is a lens at the conjugate foci of which are placed the mirrors of the two galvanometers. Two motions are in this way imparted to the spot of light, (1) a horizontal motion proportional to the temperature of the sample and (2) a vertical motion proportional to the difference in temperature between the sample and the neutral body. The resulting curves are known as differential curves (see Lesson VII, pages 10 and *seq.*)

In recent models the apparatus has been simplified and made more compact

(Figs. 43 and 44) by placing the galvanometers so near each other that the lens L, Figure 42, could be omitted and the entire instrument placed in a metallic or wooden case (Fig. 44.)

The connections between the sample and the neutral body and between these and the galvanometers are made, as first suggested by Roberts-Austen, and as clearly shown in Figure 45. In this illustration galvanometer G_1 corresponds to galvanometer G_2 of Figure 42 and galvanometer G_2 to galvanometer G_1.

ELECTRIC FURNACES

For the experimental heat treatment of small iron and steel samples an electric resistance furnace is extremely useful. For such purposes the Heræus platinum wound muffle furnaces (Fig. 46) are very satisfactory. The furnaces are provided with a safety device to take care of any overload and with an internal adjustable rheostat. They are made in different sizes, the inside measurements of the largest type being nine inches in length, six inches in width, and three and one half inches in height. Using 110 volt current they consume from five to fifteen amperes according to size and temperature. If care be taken never to use temperatures exceeding 1000 deg. C. for any great length of time, and, preferably, never to exceed 1000 deg., the furnace will be found very durable. The use of cheaper furnaces wound with base metals is a doubtful economy as frequent rewindings are required while the maximum temperature that can be safely used with such furnaces is fully 200 deg. C. lower than with platinum resistance furnaces.

LESSON I

PURE METALS

Microstructure. — When a properly prepared sample of a pure metal is examined under the microscope, the revealed structure generally presents the appearance of a polygonal[1] network (Figs. 1 and 2), an indication that the metal itself is composed of

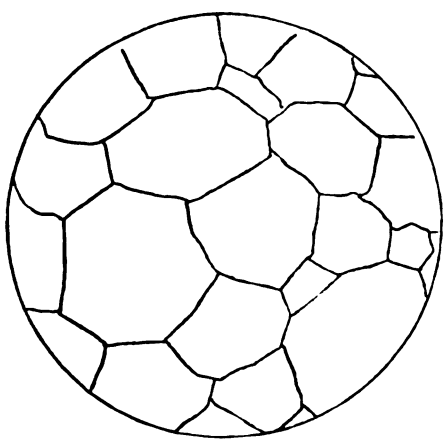


Fig. 1. — Pure gold. Cast.
Magnified 50 diameters. (Andrews.)

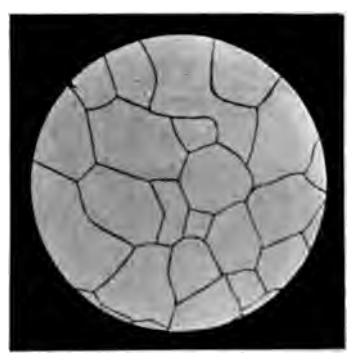


Fig. 2. — Pure copper.
Magnified 8 diameters.
(Houghton.)

irregular polyhedral[2] grains, each mesh or polygon of the network representing a section through a polyhedron.[2]

Crystallization. — When a substance passes from the liquid to the solid state, the process of solidification is generally accompanied by crystallization, i.e. the molecules of the substance so arrange themselves as to form small solids of regular geometrical outlines, such as cubes, octahedra,[3] etc. Each of these *spontaneously* formed symmetrical solids is called a crystal and any substance made up of crystals is said to be crystalline.

Crystals possess the property of breaking more readily in one or more directions. This property is called "cleavage." The planes of cleavage or direction of easy rupture are generally parallel to the faces of the crystals. A cubic crystal, for instance,

[1] A polygon is a closed geometrical figure with straight sides (necessarily three or more).

[2] A polyhedron (plural, polyhedra or polyhedrons) is a closed geometrical solid bounded by plane (smooth) faces (necessarily four or more).

[3] An octahedron (plural, octahedra or octahedrons) is a geometrical solid (a polyhedron) bounded by eight plane faces.

splits readily in three planes parallel to the three sets of faces of the solid. In Figure 3, ABC, DEF, and GHI indicate the cleavage planes of a cubic crystal. The direction of its cleavage planes constitutes the orientation of the crystal.

Solid substances which are not crystalline are said to be "amorphous." They are characterized by the absence of any symmetrical grouping of their molecules. Glass is a good example of an amorphous substance.

Idiomorphic Crystals. — When the fluidity of a substance and other conditions are such that the formation and growth of the crystals are given free play, perfect (and

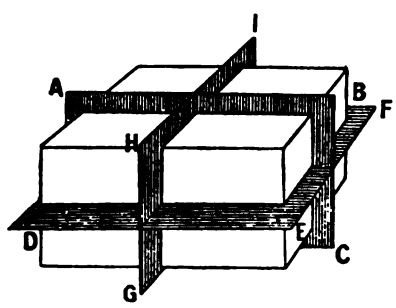


Fig. 3. — Cleavage planes. (Mellor.)

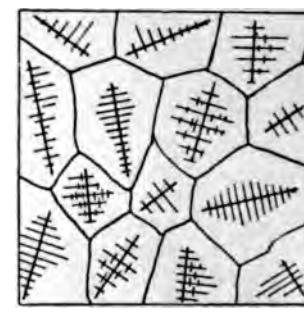


Fig. 4. — Crystallization from centers. (Desch.)

sometimes very large) crystals are produced. These perfect crystals, with faultless geometrical outlines, perfect cubes for instance, are called "idiomorphic" crystals.

Allotrimorphic Crystals. — When the free development of crystals is hindered by less favorable crystallizing conditions, such for instance as collision or contact with other crystals, likewise in process of formation, the regular external form is not preserved and the resulting imperfect crystals are called "allotrimorphic" crystals, also, but more seldom, "anhedrons" or faceless crystals. Such crystals are said to have taken their shape from their surroundings. It should be noted, however, that allotrimorphic crystals, like idiomorphic crystals, are composed of crystalline matter. An allotrimorphic crystal may be regarded as resulting from the mutilation of an idiomorphic crystal, the mutilation affecting the external shape only, and not the crystalline character of the substance.[1]

Crystallization of Metals. — Metals when they solidify generally give rise to the formation of allotrimorphic crystals. The explanation for this is to be found in the fact that crystallization sets in simultaneously at many different centers (see Fig. 4). From each center a crystal grows through successive addition of crystalline matter similarly oriented, until meeting with other surrounding crystalline growths, radiating from other centers, the free development of its external form is arrested. The polygonal networks shown in Figures 1 and 2, representing the structure respectively of pure gold and pure copper, do not indicate, therefore, cleavage planes, i.e. outlines of true crystals, but merely boundaries or junction lines between adjacent crystalline growths or "grains." They mark the regions where neighboring crystalline growths collided with resulting distortion of their external forms.

[1] Crystalline groups or aggregates of allotrimorphic crystals are sometimes called "crystallites" while if they assume some distinct form they may be further described as "dendrites" or "tree-like," "fern leaves," "star-like" crystallites, "crystalline grains," etc.

Grains of Metals. — If crystallographers were interested in the constitution and structure of metals they would undoubtedly refer to the small polyhedral grains of which they are composed as allotrimorphic crystals. This expression, however, although the only scientifically correct one, does not appeal to metallurgists, who generally call these imperfect crystals "crystal grains," "crystalline grains," or even simply "grains." The expression crystalline grains which is quite common appears satisfactory since it suggests the two main facts to be remembered as to the nature of the grains, (1) that they are not perfect crystals and (2) that they are nevertheless crystalline. Dana himself writes that cast iron is made up of *crystalline* grains. He says further: "Crystallization produces masses made of crystalline grains when it cannot make distinct crystals." Nor is there very great objection if, for the sake of brevity, the word grain alone be used, bearing in mind once for all the crystalline character of metals.

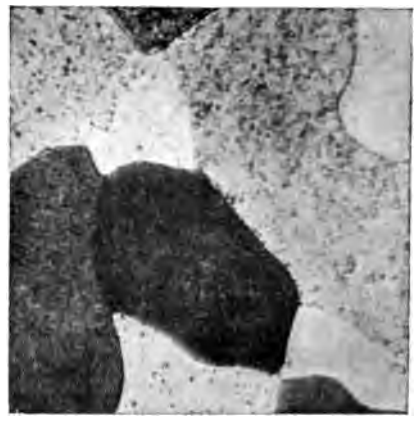


Fig. 5. — Pure platinum.
Cast. Magnified 120 diameters.
(Andrews.)

To render the polygonal boundaries of crystalline grains visible under the microscope the highly polished metallic surface must generally be treated by an acid or some other chemical reagent capable of dissolving or corroding the metal, with or without deposition of a film of some precipitated matter. According to Ewing these boundaries are made evident by the differential action of the acid which produces differences of level by attacking one grain more energetically than its neighbors. Each of the short sloping surfaces which connect one grain with another appears black under vertical illumination because it does not reflect the light back into the tube of the microscope.

Crystalline Orientation of the Grains. — A slight chemical attack or etching of the polished samples brings out merely the polygonal structure described and illustrated in the preceding pages. If the etching be somewhat deeper, however (through the use of a stronger reagent or because of a longer attack), it is observed that the polygons or meshes of the network are differently colored (Fig. 5), some appearing very dark, others less dark, others, still, brilliant. This heterogeneousness in the appearance of sections through adjacent grains is due to the fact elucidated above that *each grain, i.e. each allotrimorphic crystal, is made up of crystalline matter similarly*

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ark grains become brightly illuminated,
the light reflected by each individual
changing the direction of the incident
affords a conclusive proof of the crys-
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Pits. — By still deeper etching of the
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allization of metals such for instance as the hex-
crystallographers consider to be due to interfering
belonging to the cubic system). Again, under favor-
have been obtained in the case of several metals.

Impurities. — It is well known that the addition of surprisingly small amounts of impurities or foreign substances often affect very greatly some of the most important properties of metals, such as their strength, ductility, fusibility, electrical conductivity, etc., and we naturally look for correspondingly marked changes of structure. In order to understand this important influence of impurities upon the properties of metals it will be necessary to consider at some length the nature of the union which exists between the metal and the impurity. Let us first note that by impurity we mean a *very small proportion* of some foreign substance which may be any other metal, a metalloid, or a definite compound.

The metal or metalloid contaminating the metal may (1) remain uncombined or (2) it may combine with some (generally a small amount) of the metal to form a definite chemical compound. The uncombined contaminating metal or metalloid or resulting chemical compound may then (*a*) be soluble in the solid metal forming with it a "solid solution" or (*b*) be insoluble in the solid metal in which case it is rejected by the crystalline grains, in the form of an eutectic alloy.

The meaning of the expressions "solid solutions" and "eutectic alloys" should now be explained. As Professor Howe has well expressed it the essential features of an ordinary liquid solution are (1) a complete merging of the constituents and (2) in indefinite proportions. By complete merging is meant a union so intimate that the separate existence of the constituents cannot be detected by any physical means, such for instance as microscopic examination under the highest magnification. The homogeneity of the substance is such that it resists any physical attempt at breaking it. The merging moreover must remain complete and absolute for varying proportions of the constituents, for it is evident that if it existed only for certain well-defined proportions of the component parts, the resulting substance would be of the nature of a definite chemical compound and not of a solution.

Bearing in mind these characteristics of ordinary solutions, we find that in some substances, while passing from the liquid to the solid state, the constituents remain completely merged and in indefinite proportions. *The essential characteristics of liquid solutions are retained in the solid state.* Hence the name of solid solutions given to such substances. A common and excellent example of solid solutions is found in the case of glass in which the three usual constituents, silica, lime, and alkali, are so completely merged that their existence cannot be detected by physical means; the microscopical examination of glass under the highest magnification fails to reveal the presence of its component parts. Glass on solidifying passes from the condition of a liquid solution to that of a solid solution. Many metals likewise form on solidifying solid solutions; i.e. they solidify into a mass so absolutely homogeneous that the identity of the component metals is entirely lost. The union between some metals and metalloids also frequently forms solid solutions.

It is held by some crystallographers that in order to form solid solutions the uniting substances must be "isomorphous." that is, must be capable of yielding crystals of the same form, hence the name of "isomorphous mixtures" frequently given to solid solutions.[1] The homogeneous crystals formed by solid solutions are often called

[1] If isomorphism favors the formation of solid solutions, as it undoubtedly does, seeing that most metals are isomorphous, we naturally infer that they will readily form solid solutions. We now know that such is the case, for if metals are not generally soluble in each other (when solid) in *all proportions* there are few instances of metals entirely insoluble in each other in the solid state. The formation of solid solutions between metals is therefore very frequent.

"mixed crystals" — and that expression frequently used as an equivalent for solid solution. There are some crystallographers, however, who believe that isomorphism of the constituents is not essential to the formation between them of solid solutions, and that the use, therefore, of isomorphous mixtures as synonymous of solid solution is not warranted. The use of the expression mixed crystals is likewise to be discouraged because it suggests a mixture, and, therefore, heterogeneity, which is precisely contrary to the nature of solid solutions.

Considering now those impurities, whether metals, metalloids, or definite compounds, which form solid solutions with the metal they contaminate, it is found as might have been expected that their presence has no great influence upon the character of the structure. Suitably prepared surfaces of such impure metals still exhibit the polygonal network structure characteristic of pure metals. The small polyhedra of which the impure metal is composed, however, are now allotrimorphic

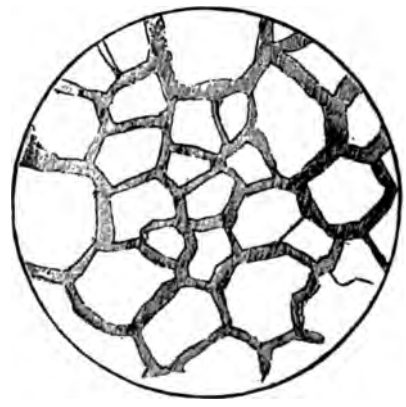


Fig. 7. — Gold containing 0.20 per cent lead. Magnified 100 diameters. (Andrews.)

crystals of a solid solution instead of a pure metal. While the character of the structure remains the same, the dimension of the grains may be markedly affected, being often increased by the presence of a small amount of impurity forming a solid solution with the metal; such for instance is the action of phosphorus on iron, to be considered later. This enlargement of the grain is generally accompanied by decreased ductility or even by brittleness.

The second group of impurities, namely those foreign substances, whether they remain or not uncombined, which do not form solid solutions with the contaminated metal may usually be readily detected under the microscope as they are generally rejected to the grain boundaries during the process of solidification (or afterwards) as shown in Figure 7. These insoluble impurities are not, however, rejected as such by the crystalline grains, but on the contrary unite *mechanically* with a small amount of the metal to form what is known as an "eutectic alloy," that is an alloy of lowest melting-point, and it is this alloy which is expelled by the solidifying grains. The formation and nature of eutectic alloys will be considered at greater length in a subsequent lesson.

It will be apparent that those contaminating substances which fail to be dissolved by the metal, may form actual membranes surrounding each grain, the mem-

branes being of the nature of an eutectic alloy. As might be anticipated, the presence of such membranes, whether continuous or not, have generally a very marked influence upon the properties of the metals, frequently decreasing their ductility, weldability, electrical conductivity, etc., and often increasing their fusibility, hardness, etc.

The rejection during solidification and subsequent cooling of those impurities which fail to be retained in solid solution by the metal, to the grain boundaries or other crystallographic planes, reveals the crystalline forms of the grains themselves. The location of these impurities affords additional evidence of the cubic crystallization of metals. It will be shown later that the cubic crystallization of iron is in this way clearly revealed.

The above remarks are of a very general character and refer more especially to the behavior of impurities while the metal solidifies. In the majority of cases no further changes take place in the nature of the constituents as the metal cools to atmospheric temperature, i.e. the constituents formed on solidification are those found in the metal after complete and slow cooling. In some instances, however, and notably in the case of iron and its usual impurities, carbon, silicon, phosphorus, manganese, and sulphur, some important changes take place at temperatures considerably below the solidification point of the metal which will be duly described at the proper time.

Influence of Thermal Treatment. — The size of the crystalline grains of pure metals varies in different metals even when cast and cooled under identical conditions. Their dimension is generally affected also by the rate of cooling during solidification, and, therefore, by the size of the casting, since a large casting will cool more slowly than a smaller one.

The common belief is that the prolonged exposure of pure metals to a high temperature (annealing) tends to enlarge the grains, the enlargement being the greater the higher the temperature, the longer the time of exposure, and the slower the cooling. While such growth undoubtedly takes place in the case of commercial and, therefore, impure metals, at least after straining, it is held by some metallurgists that in absolutely pure metals the grain will not grow on annealing even after straining.

This view is based upon a theory brilliantly conceived by Ewing and Rosenhain and supported by the results of skilfully conducted experiments. These scientists argue that even so called pure metals always contain a certain amount of impurities, and that even a very minute amount of impurity would suffice to form a thin but practically continuous film of eutectic in the crystalline boundaries. They contend "that there is constant diffusion from the surface of the crystal into the eutectic and equally constant re-deposition of metal upon the crystal from the eutectic. If there are several crystals in contact with the same eutectic, there will be, under some conditions, a state of dynamic equilibrium between them, the amount dissolved from each being exactly counterbalanced by the amount deposited upon it; if, however, there is any difference in their solution pressure in respect to the eutectic, then the less soluble will grow at the expense of the more soluble. The metal constituting the eutectic films being much nearer its melting-point than the rest of the mass, would thus be favorable to comparatively rapid diffusion, but the rate of such diffusion, and, consequently, the rate of growth of crystals, would be enormously increased by heating the metal to a temperature above the melting-point of the eutectic in question."

The theory proposed depends upon the existence of a difference in the solubility of the two crystal faces in contact with the eutectic film. The only difference between these two faces is, apparently, in the orientation of the crystalline elements, but this difference is sufficient, in the writers' opinion, to produce a difference in their rate of solution in the eutectic film, assuming that it causes a such marked difference in their solubility in the etching acid, which, as is well known, always [illegible]

grains much more readily and deeply than neighboring ones whose elements have another orientation. To account for the influence of the orientation of the elements upon the solubility of the crystals, the authors suggest to extend to alloys the electrolytic theory of solution. "Such differential actions," they say, "may most probably be attributed to differences of electrical potential in the surfaces involved. If we accept this view of the matter, then the diffusion across films of eutectic becomes a case of electrolysis."

This theory explains why only strained crystals of the metals examined will grow, while unstrained crystals show no tendency to change, even at high temperatures. "The explanation, on the electrolytic theory, is that in the unstrained state the crystals are surrounded by practically continuous films of eutectic, and that electrolysis only becomes possible when severe distortion has broken through these films in places, allowing the actual crystals to come into contact; the electrolytic circuit would then be for each pair of crystals, from one crystal to the other by direct contact and back through the eutectic film."

If the authors' conception be true, recrystallization by annealing in a perfectly pure metal would not occur but, as they rightly say, it is almost hopeless to obtain a sample of metal sufficiently pure to prove or disprove the theory. They argue, however, that if the growth of crystals is due to the presence of a eutectic film between them, the absence of such film would be a barrier to all such growth, and that a weld between two clean-cut surfaces should show no growth of crystal across the weld. This they actually proved to be so in the case of lead.

If they are right, it likewise follows that in metals contaminated by impurities with which they form solid solutions there should be no growth of grains on annealing, because of the absence of the needed eutectic film.

The remarkable crystalline growth of very low carbon steel after severe straining followed by annealing at suitable temperatures, described in another lesson, is a striking instance of the action of straining (cold working) in promoting grain growth in subsequent annealing.

Notwithstanding Ewing's and Rosenhain's strong argument, satisfactory evidences are still lacking in support of the contention that both straining and the presence of impurities are necessary conditions to grain growth on annealing. So far as the matter has been investigated it does seem that the grain of a pure metal will not grow unless it has been previously strained, but that it must also contain some eutectic forming impurities has not been satisfactorily demonstrated.

Influence of Mechanical Treatment. — Metals are frequently subjected to powerful pressure exerted by rolls, presses, hammers, etc., with a view of producing metallic objects of desired shapes. This treatment affects the structure and, therefore, the properties of the metal. Roughly speaking such vigorous kneading has a tendency to reduce the size of the final grains, either through preventing the formation of large grains or by breaking up or distorting preexisting grains. A smaller grain in turn generally implies greater ductility (provided it be not distorted) and often greater strength. The effect of work upon the structure and properties of commercial iron and steel will be duly considered in these lessons.

Examination

I. Explain the formation and nature of the polyhedral grains of which pure metals are composed.

II. Explain the meaning of (1) solid solutions, (2) isomorphous mixtures, and (3) mixed crystals.

III. Describe the changes of structure, if any, produced in metals by the presence of small quantities of impurities.

LESSON II

PURE IRON

Chemically pure iron is not a commercial product. It can only be obtained in small quantities by carefully conducted laboratory manipulations when, even with the most refined care, it is quite impossible to produce it absolutely pure. Until quite recently the purest commercial iron was of Swedish origin and contained as much as 99.8 per cent of iron. A commercial product known as "American Ingot Iron"[1] is now manufactured which the makers claim to contain 99.94 per cent of

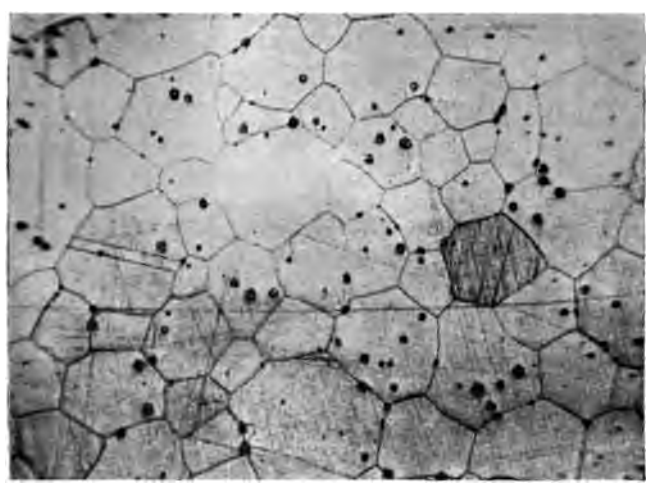


Fig. 1. — Electrolytic iron. Magnified 75 diameters. Slightly etched.
(Sherard Cowper-Coles.)

iron. Iron, or rather very low carbon steel, of a high degree of purity is also produced at the present time through refining in electric furnaces. Finally iron has been obtained in relatively large quantity, by electrolytic deposition, of a degree of purity exceeding 99.9 per cent iron.

Microstructure. — When a sample of nearly pure iron is suitably prepared and examined under the microscope some regions can readily be found absolutely free

[1] The expression "ingot" iron is applied to iron containing very little carbon, obtained molten and, therefore, cast, after removal from the furnace, whereas by wrought iron is meant iron (also generally low in carbon) obtained pasty and, consequently, always containing a certain amount of slag. Barring the presence of slag in wrought iron, both ingot iron and wrought iron may have identical chemical compositions. The expression ingot iron is seldom used in the United States, where iron obtained in a liquid state, and containing little carbon, is called low or very low carbon steel, or mild, very mild, extra mild, steel, or again soft, very soft, dead soft steel.

from carbon and slag and exhibiting, therefore, the structure of the pure metal. Such structure is illustrated in Figure 1 after a slight etching of the polished surface. It will be noted that it is similar to the structure of pure gold and of pure copper described in the preceding lesson: like gold and copper and, indeed, like most metals

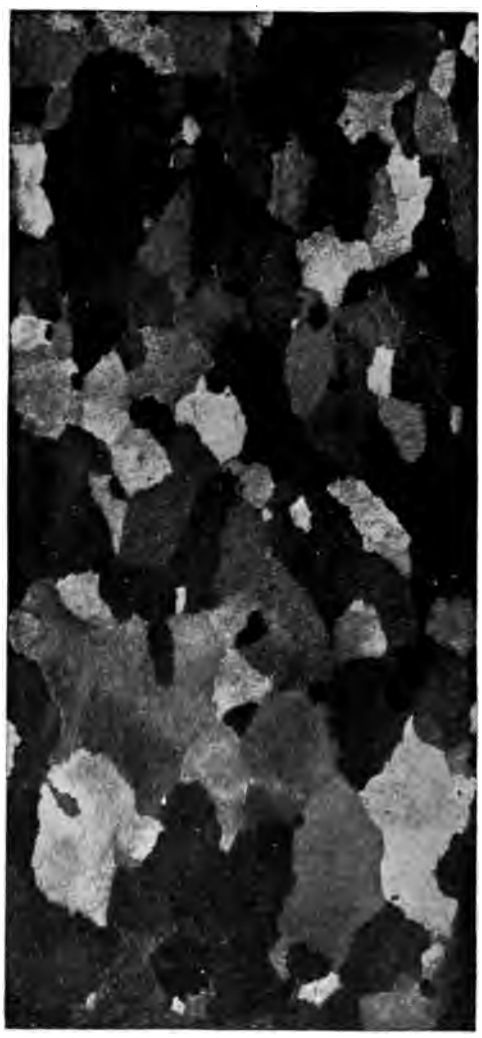


Fig. 2. — Ferrite grains. Natural size.
Etched 10 minutes in nitric acid (1 to 10 water).
(Stead.)

iron is made up of polyhedral crystalline grains (allotrimorphic crystals). Upon deeper etching the dissimilarity, as to coloration, of adjacent iron grains is clearly brought out as shown in Figure 2. As explained in Lesson I, this appearance is due to the fact that the grains of iron are composed of crystalline elements having the same orientation in the same grain but different ones in different grains.

Cubic Crystallization of Iron. — A still deeper etching indicates clearly the cubic character of the crystallization of pure iron. This is illustrated diagrammatically in

Figure 3 and by means of a photomicrograph in Figure 4. It will be noted that the etching pits are similarly oriented in the same grain but that the orientation in adjacent grains differs. As seen in Figure 3, the etching figures may appear as triangular wedges. This occurs when the section cuts the small cubes of a grain at a certain

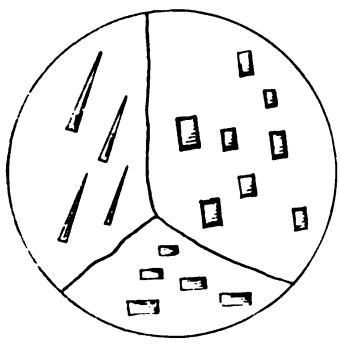


Fig. 3. — Etching pits in iron. (Desch.)

Fig. 5. — Silicon steel, 4.5 per cent silicon. Magnified 60 diameters. Part of a single grain. Etched three hours in nitric acid (1 to 10 water). (Stead.)

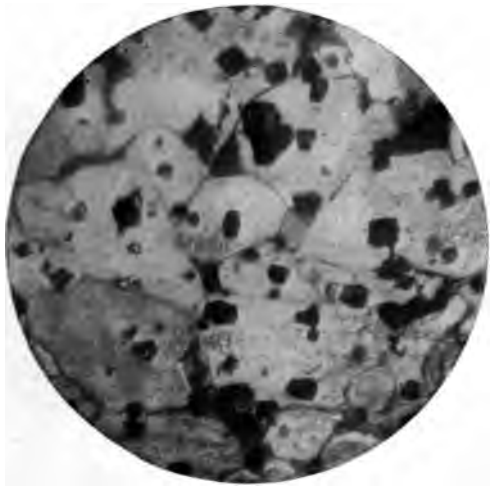


Fig. 4. — Etching pits in ferrite. (J. F. Hoyland.)

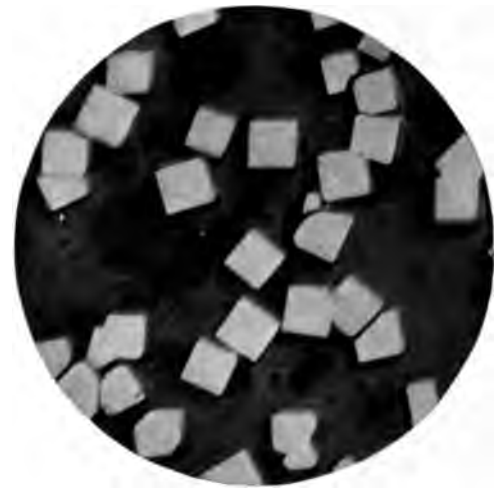


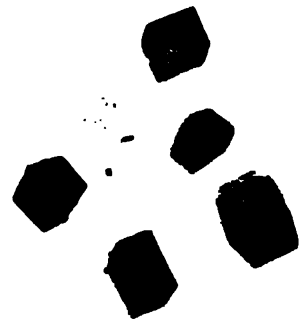
Fig. 6. — Cubic crystals of iron. Magnified 250 diameters. Obtained through the reduction of ferrous chloride. (Osmond.)

angle, i.e. when it cuts obliquely a corner of each cube. This cubic structure is further illustrated in a remarkable manner in Figure 5, in the case of iron containing 4½ per cent of silicon after etching three hours in dilute nitric acid. The photograph shows a portion of a single grain, hence the constancy of orientation noted. The presence of so much silicon apparently favors the development of a coarse cubic crystallization.

Osmond, through the reduction of ferrous chloride and the crystallization of the

... perfect isolated cubic crystals (Fig. 6). Finally ... separated by Stead from a large granule of phos... ...ication of the cubic crystallization of iron is found ... ...es Fig. 8), generally resembling pine trees, in ... steel, under conditions, therefore, favorable to ... these crystallites being composed of small octa... ...ic system. Finally it will be shown later that ... impurities generally present in commercial ... ...ic crystallization of iron.

... have been given to the constituents of iron and ... ferrite, considered as a microscopical con-



... crystals of phosphoretic iron. ... meters. Phosphorous 0.75 ... 0 per cent. (Stead.)

... name suggested by Professor H. M. Howe and ... therefore, is composed of polyhedral crystalline ... subsequent lessons that the ferrite of commercial ... iron, but rather a solid solution of iron holding ... s, and possibly other impurities.

... of the crystallization of iron is complicated by ... ...ons of that metal.

... sudden changes in some of the properties of a

... by Sorby, who was the first scientist to describe the

... on the Uniform Nomenclature of Iron and Steel, ferrite ... solution in the case of commercial grades of iron and ... manganese, phosphorus, and of some other rarer ele... ...bon, if any." There is no conclusive evidence, how... ...s it likely that iron retains any manganese in solid ... purity is present. (See Lesson VI on Impurities in ... ...n ferrite consists only of pure iron it should be called

Fig. 8. — Iron crystallite about half natural size. (Tschernoff.)

critical temperatures, without any change of state or
... Polymorphism, sometimes used as the equivalent of allo-
... to the property of some substances of crystallizing in
... allotropy does not necessarily imply such property.
... undergo allotropic changes. It is a matter of common knowl-
... sulphur exists under two distinct conditions, namely, as pris-
... octahedral sulphur, the prismatic form being the one stable
... octahedral, the stable form below that critical tempera-
... octahedral sulphur it begins to change into the prismatic form at
... deg., and, likewise, on cooling, prismatic sulphur begins to
... form at that temperature. Many of the physical properties of
... (volume, specific heat, heat of combustion, etc.) undergo sudden
... substance passes from one allotropic form to another.
... temperatures which mark the passage of one allotropic form into
... evolutions of heat take place on cooling and spontaneous ab-
... heating. These thermal disturbances indicate a change of in-
... when not accompanied by changes of state or by chemical
... of allotropy. The usual method of detecting the existence of
... points will be described in another lesson.
... discovery of the existence of two thermal critical points
... existence of iron in at least three allotropic forms. The two
... pure iron correspond respectively to about 875 and 750 deg.
... exists in a certain allotropic condition known as γ (gamma)
... deg. is reached iron passes from the γ form to another
... beta) iron and at 750 deg. β iron in turn changes into a
... alpha) iron, which remains the stable form at atmospheric
... changes occur on heating, that is iron passes from the α
... form on passing through the two critical tempera-

... passage of one allotropic form into another implies
... sudden changes in many of the physical properties of
... iron differ widely in regard to many of their physical
... in this lesson, however, to inquire into the possible
... which may exist between the three allotropic conditions

... graphy published by the Iron and Steel Institute in 1901
... to undergo without change of composition a change of chem-

... a change of internal energy occurring in an element at
... by a change of state." In the above definition the word
... place of element, for allotropic changes are not confined to
... and possibly solid solutions, may undergo allotropic trans-

... defines allotropy "a change in the properties of an element
... accompanied by a change of internal energy. It is due in
... a change in the number or in the arrangement of the atoms of
... varieties are sometimes termed 'isomerides.'"
... other writers, while admitting the existence of a lower critical point in
... indicates an allotropic change, being consequently inclined to deny the
... This opinion will be considered and the allotropy of iron treated at greater
... length.

of iron, postponing until a later lesson a description of the modification of the other properties.

Osmond and, later, Osmond and Cartaud have carefully investigated the difficult problem of the crystallization of the different allotropic forms of iron. Their conclusions were (1) that the three allotropic forms of iron crystallize in the cubic system,[1] (2) that octahedra are the prevailing crystalline forms of gamma iron, (3) that the cube is the prevailing form of beta and of alpha iron, (4) that beta and alpha iron are capable of forming isomorphous mixtures (solid solutions), (5) that gamma iron does not form isomorphous mixtures with beta or alpha iron.

We also have the statement of Osmond that the transformation of gamma iron into beta iron appears to include a change in the planes of symmetry, at least in carburized iron.

Again it has been shown by Osmond and confirmed by other investigators that the occurrence of twinnings is frequent in gamma iron, while beta and alpha iron are free from it. By twinning is meant the grouping of two or more crystals or parts of crystals in such a way that they are symmetrical to each other with respect to a plane between them (the twinning plane) which plane, however, is not a plane of symmetry for either crystal.

Twinnings are also produced through pressure or other stress tending to strain the crystals especially when the straining is followed by annealing. In Figures 9, 10, and 11 are shown twinnings respectively in marble (due to pressure), in brass, and in gamma iron. The straight parallel lines and bands running through the polyhedral grains indicate the twinning planes.

From these conclusions which have been confirmed by the results obtained by other investigators, it follows that the allotropy of iron could not be proved by its crystallography, since the thermal critical points are not accompanied by changes in the crystalline form of iron. While, however, in the instances of allotropy which have been noted and studied allotropic changes are generally accompanied by changes of crystalline forms, it does not by any means follow that any allotropic transformation must necessarily imply a crystalline change.

Bearing in mind the existence of three allotropic conditions of iron, let us follow in our imagination the crystallization of iron during solidification and its subsequent cooling to atmospheric temperature. On solidifying, polyhedra or allotrimorphic crystals of gamma iron are formed, which according to Osmond are chiefly made up of octahedral crystals. Were it possible to examine a section of the solidified metal at such a high temperature the usual polygonal network structure characteristic of pure metals would be revealed. Upon further cooling below the solidification point, no change of crystalline form should take place until the first critical temperature (875 deg. C.) is reached when the iron changes from the gamma to the beta condition.

Does this allotropic change affect the preexisting crystallization of gamma iron or does it consist merely in a transformation *in situ* of each crystalline grain of gamma iron into a grain of beta iron, retaining the original external form of the gamma grain, and leaving undisturbed, therefore, the polygonal structure observed under the microscope? It may reasonably be supposed that the allotropic transformation takes place without affecting the external form of the crystalline grains, but in view of

[1] In Le Chatelier's opinion there is no proof of the cubic form of gamma iron. He thinks that the facts observed are contrary to that hypothesis and that it is more probable that gamma iron is rhombohedral or orthorhombic.

Osmond's statement that the octahedron is the prevailing crystalline form of gamma iron and bearing in mind that the small crystals revealed by suitable etching of pure iron are generally cubic, we naturally infer that the octahedral character of each grain of gamma iron has been obliterated, the small octahedral elements of gamma

Fig. 9. — Twinnings in marble (caused by pressure). Magnified about 5 diameters. (Bayley.)

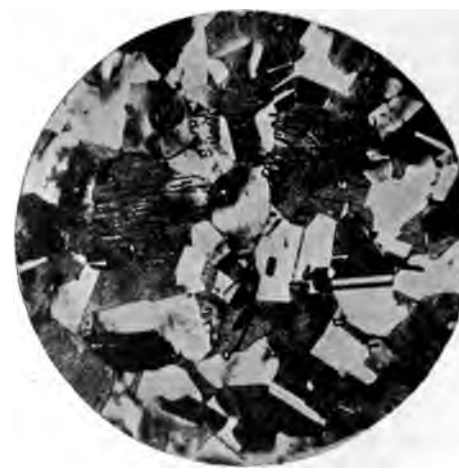


Fig. 11. — Twinnings in gamma iron. Magnified 200 diameters. (Osmond.)

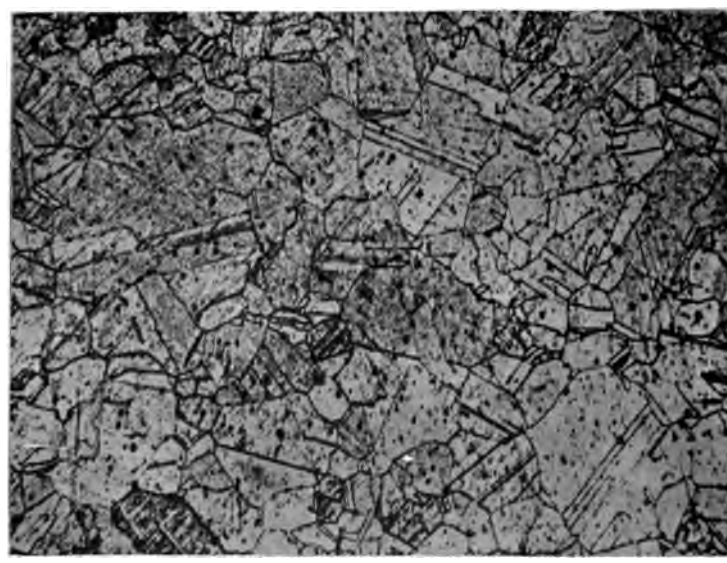


Fig. 10. — Twinnings in brass. Magnified 100 diameters. (Law.)

iron having been replaced by small cubic elements of beta (and later of alpha) iron. These conclusions, however, should be accepted with reserve, as we lack evidences of a very conclusive character. It has been shown that the change of gamma iron into beta iron is accompanied by an abrupt expansion of the cooling metal which expansion is followed by the normal contraction of cooling substances. We infer from

this that, momentarily at least, each grain of beta iron occupies more space than its gamma iron progenitor.

At 750 deg. C. or thereabout, the iron passes from the beta to the third or alpha form. We may here ask the same questions as to the probable effect of this change upon (1) the outward form of each beta grain and (2) upon the internal crystalline structure of each grain. Since both beta and alpha iron crystallize in the cubic system, the cube being the prevailing crystalline form of both, and since, according to Osmond, they are isomorphous, that is capable of forming solid solutions, it seems probable that the change of beta to alpha iron affects neither the external form nor

Fig. 12. — Polished sample of iron, etched, then reheated in hydrogen to 950 deg. C. and slowly cooled. Magnified 600 diameters. (Kroll.)

the internal crystalline arrangement of the beta grains; in other words that each small cubic element of beta iron is converted bodily (although probably gradually and not abruptly) into a cubic element of alpha iron.

If the above represents the real mechanism of the allotropic changes, it will be evident that the polyhedral grains revealed through the etching of polished sections of pure iron were formed during solidification and consisted originally of gamma iron, these grains having retained their external shape while undergoing allotropic transformation, but having probably undergone at the upper critical point an internal change, the octahedral form of the crystalline elements having been replaced by the cubic form.

Some experimental evidences, however, have recently been brought forward which would lead to somewhat different conclusions. Kroll in a valuable and suggestive contribution expresses his belief that he has been able to develop in a sample of nearly pure iron three distinct polygonal networks, corresponding respectively to the crystallization of gamma, beta, and alpha iron. This interesting composite structure is illustrated in Figure 12. It was obtained in heating a polished section of pure

iron in a current of hydrogen gas, when it was found that the three polygonal structures were revealed. If the meaning of this structure is correctly interpreted by Kroll, it, of course, points to marked crystallographic changes closely related to the thermal points of Osmond. As Professor Le Chatelier rightly says, however, the accuracy of Mr. Kroll's conclusions might be questioned, because changes of structure must take place on cooling as well as on heating so that five and not three network structures should be observed.

Rosenhain and Humfrey by straining a bar of iron heated to a high temperature at the center (the temperature, therefore, decreasing towards both ends) have made evident the existence of three distinct kinds of distortions with sharp lines of demarcation between them, corresponding in all probability to the distortion respectively of gamma, beta, and alpha iron. The estimation of the temperature of different portions of the bar by means of fusible salts appears to sustain the authors' contention thus furnishing an additional support, and a substantial one, to Osmond's brilliant theory of the allotropy of iron.

Nevertheless information of a more positive and concordant nature is still needed to settle to the satisfaction of all the question of the relation between the thermal critical points of pure iron and possible crystallographic changes.

While the allotropy of iron is of little industrial importance in the case of iron and of low carbon steel it becomes, on the contrary, of very great moment in high carbon steel, for it is probably the cause of that invaluable property possessed by such steels of becoming intensely hard upon rapid cooling from a sufficiently high temperature. The question of the hardening of steel will be duly considered in these lessons.

Influence of Impurities. — Commercial iron is always contaminated by the presence of at least five elements, namely, manganese, silicon, phosphorus, sulphur, and carbon, generally referred to, although often wrongly, as impurities. The important question of the influence of these substances upon the structure, and, therefore, upon the properties, of iron and steel will be fully considered in another lesson, when it will be shown that these elements form definite compounds with iron, FeSi, Fe_3C, Fe_3P, or with each other, Mn_3C, MnS, and that some of these compounds, FeSi, Fe_3P, are retained by the iron in solid solution, while others, Fe_3C, Mn_3C, MnS, are rejected to the boundaries of the crystalline grains or along other crystallographic planes, the former two giving rise to the formation of eutectoid mixtures. This behavior of the impurities of iron and steel conforms with the general behavior of impurities described in Lesson I.

Influence of Heat Treatment. — The size of the grains of iron is affected, like that of other metals, by the temperature from which it cools, the length of time it is kept at that temperature, the rate of cooling, etc., in other words by what is known as its heat or thermal treatment. Generally speaking it may be said that the higher the temperature the larger the grains and also that the slower the cooling the larger the grains. These results might have been anticipated if it be considered that slow cooling from a high temperature is a condition favorable to the formation and growth of crystals. As stated in Lesson I, however, it is not certain that pure metals undergo any crystalline growth on reheating (annealing) unless they have previously been strained and, indeed, unless they contain also a trace at least of impurities. For similar reasons we may doubt the existence of any crystalline growth in annealing chemically pure iron or indeed impure iron unless it has been previously strained.

The influence of heat treatment upon the structure and physical properties of commercial irons and steels will be dealt with at length in these lessons.

Influence of Mechanical Treatment. — Like that of other metals the structure of iron is affected by mechanical work. Undisturbed cooling being a necessary condition to the free development of crystals, it will be evident that if the metal be vigorously worked, that is subjected to powerful mechanical pressure, while cooling from a high temperature, the formation of crystalline grains will be greatly hindered or preexisting crystals broken or distorted. The important influence of work upon the structure (and therefore upon the properties) of iron and steel will be duly considered in these lessons.

Straining of Iron. — Slip Bands. — Ewing and, later, Ewing and Rosenhain through some skilfully conducted experiments and convincing reasoning have revealed the character of the strain produced in a pure metal by the action of a stress

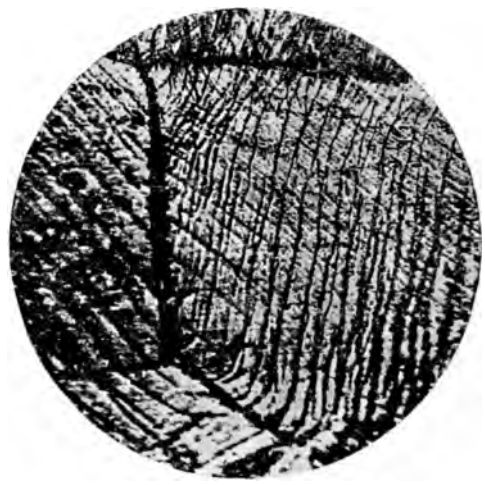


Fig. 13. — Slip bands in Swedish iron strained by tension. Magnified 400 diameters. (Ewing and Rosenhain.)

which may eventually cause its rupture. This will be briefly described here in the case of pure iron.

Polished sheets of metals were strained very gradually while being examined under the microscope. When the yield point is reached, i.e. when plastic deformation begins to occur, black lines are seen to cross the crystalline grains of which the metal is made up. These lines are generally quite straight and are parallel in the same grains but have different directions in different grains. Figure 13 shows the appearance under vertical light of Swedish iron, strained by tension, magnified 400 diameters.

As the strain increases other systems of lines, inclined to the first, make their appearance and eventually two, three, and even four systems of intersecting lines may be seen in each grain.

These lines are not cracks but steps in the surface, which steps are due to slips along the cleavage or gliding planes of the crystals. In Figure 14, AB represents the

polished surface of two grains, C the junction line between these two grains. The pull takes place in the direction of the arrows.

Yielding occurs by finite amounts of slips at a limited number of places, *a*, *b*, *c*, *d*, *e*, resulting in short portions of inclined cleavage or sliding surface appearing black under the microscope, because they do not send back any light into the tube. By oblique light some of these slip bands appear black while others are bright. When the surface is rotated some of the bands which were black become bright and *vice versa* owing to the change of their position in regard to the incidence of the light,

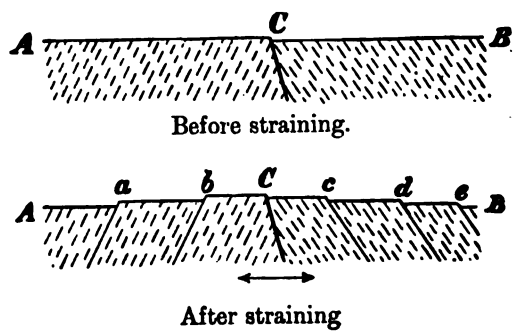


Fig. 14. — Diagram illustrating the effect of strain upon the structure of metals and alloys. (Ewing and Rosenhain.)

which is conclusive proof that the black lines are not cracks, but inclined surfaces as described above.

It is seen then that, contrary to the general belief, metals remain crystalline after the severest strain, and that the flow or plastic strain in metals is not a homogeneous shear such as occurs in the flow of viscous fluids, but is the result of a limited number of separate slips, the crystalline elements themselves undergoing no deformation.

Examination

I. Describe the microstructure of pure iron as revealed by the microscope (1) after a slight etching of the polished surface, (2) after a deeper etching, and (3) after a still deeper etching.

II. Give some evidences of the cubic crystallization of iron.

III. Describe the allotropy of iron.

LESSON III

WROUGHT IRON

Wrought iron is the name given to commercial iron free enough from carbon and other impurities to be malleable when such metal is manufactured through the reduction of iron ores or the refining of cast iron at a temperature so low that it is obtained in a pasty condition and, therefore, mechanically mixed with a considerable amount of the slag formed during the operation.

When the refining treatment is conducted at a temperature sufficiently high to deliver the resulting products in a molten condition, the refined metal which is then free from slag is called steel. Wrought iron and steel may otherwise have identical chemical composition, although usually steel contains more manganese and less silicon than wrought iron, often more carbon and less phosphorus.

Commercial iron which is not malleable is called cast (pig) iron. The modern method of producing wrought iron consists in refining cast iron in a non-regenerative reverberatory furnace (the puddling furnace), while the refining of cast iron for the production of steel is conducted (1) in the Bessemer converter or (2) in a regenerative reverberatory furnace (the Siemens open-hearth furnace). Cast (pig) iron is the result of smelting iron ore in blast-furnaces.

Chemical Composition. — Wrought iron contains, besides an appreciable amount of slag, a small proportion of carbon and small quantities of the usual impurities, manganese, silicon, phosphorus, and sulphur.

Microstructure of Longitudinal Section. — Upon being withdrawn from the puddling furnace, the white hot, pasty balls of wrought iron are subjected to vigorous forging or squeezing, thus expelling a large amount of slag and firmly welding together the particles of iron. Through additional heating and forging or rolling the metallic mass is converted into such elongated shapes as blooms, billets, bars, etc. These operations so affect the structure as to impart unlike appearances to sections cut longitudinally, i.e. in the direction of forging or rolling, and sections cut transversally, i.e. at right angles to that direction. The microstructure of the longitudinal section of a wrought-iron bar is shown in Figures 1 and 2. From our knowledge of the chemical composition of wrought iron we should be able to anticipate its microstructure. The ground mass or matrix of the metal consists of polyhedral crystalline grains of iron, that is of ferrite, similar in every respect to the crystalline grains of pure iron and of pure metals in general described in Lessons I and II. The ferrite of wrought iron, however, as explained in Lesson II, is not pure iron but rather a solid solution of iron in which are dissolved small quantities of silicon, phosphorus, and other minor impurities. This true character of commercial ferrite is too often lost sight of and the constituent considered as pure iron. The difference in coloration between adjacent grains of this commercial ferrite should be noted, and will of course be readily understood in view of the explanation given in Lesson I to account for this phenom-

enon. Many irregular black lines, varying much in thickness and length, but all running in the same direction are clearly seen. These lines indicate the location of the slag which has assumed the shape of fibers or streaks running in the direction of the rolling or forging, thus imparting a fibrous *appearance* to the metal.

The presence of a small amount of carbon in wrought iron results in the occurrence of a new constituent in the shape of small dark particles located between some of the grains. Under low magnification these carbon-holding particles are not readily distinguishable from slag particles and as this carburized constituent is not a very important one in the case of wrought iron it seems advisable to postpone its description.

Fig. 1. — Wrought iron. Longitudinal section. Magnification not stated. (Longmuir.)

Fig. 2. — Wrought iron. Longitudinal section. Magnified 100 diameters. (Boynton.)

Summing up, wrought iron consists essentially of a mass of ferrite containing many elongated particles of slag.

Microstructure of Transverse Section. — The microstructure of the transverse section of a wrought-iron bar is illustrated in Figures 3 and 4. Like the structure of the longitudinal section, it consists of a polygonal network, indicating that the metal is made up of polyhedral crystalline grains of ferrite. The slag, however, which in the longitudinal section occurred as fibers running in a direction parallel to the rolling or forging, here assumes the shape of irregular, dark areas, corresponding to the cross sections of the slag fibers. It will be noted that in both the longitudinal and transverse sections the ferrite grains are equiaxed, that is, they show no sign of having been elongated in the direction of the rolling. It was thought for many years that wrought iron actually had a fibrous structure and, indeed, the number of persons still holding this view is surprisingly large. Many valuable properties were attributed to puddled iron on account of its "fibrous structure" which were denied to steel because of its "crystalline structure." The microscope has summarily disposed of this erroneous belief in showing that the ferrite constituting the bulk of wrought iron is in no way different from the ferrite forming the bulk of low carbon steel. Both are equally crystalline.

ag. — The essential chemical constituents of the slag
race and retained in part by the iron are iron oxides,
as (FeO), oxide of manganese (MnO), silica (SiO_2), and
these the oxides of iron and manganese are basic in their
ea and phosphoric acid are acid. These bases and acids
to form neutral compounds: silicates and phosphates of

Slag. — It will be seen in Figures 1 and 2 that the slag fibers
at least two constituents, a dark and a lighter one, the light

Fig. 3. — Wrought iron. Transverse section. Magnification not stated. (Longmuir.)

Fig. 4. — Wrought iron. Transverse section. Magnification not stated. (Guillet.)

constituent moreover often occurring in the form of small rounded areas. This structure of the slag is shown more clearly and on a larger scale in Figure 5. We are naturally led to speculate as to the nature of these two distinct constituents of the slag, and in view of our knowledge of the chemical composition of slag as stated in the preceding paragraph we are tempted to conclude that one of the constituents is a silicate of iron and manganese while the other is a phosphate of the same bases. The accuracy of this deduction, however, remains to be proven.

According to Matweieff the rounded light areas consist of iron oxide mixed or not with manganese oxide, and the darker background of silicate of iron and manganese.

Matweieff recommends the following method to distinguish between the different constituents of slag. The polished sample placed in a tube is heated and treated by a current of pure hydrogen which causes the reduction of the metallic oxides while the silicates are unaffected. To detect the presence of ferrous oxide (FeO) the sample heated to a red heat is acted upon by steam, a treatment resulting in oxidizing the ferrous oxide into magnetic oxide (Fe_3O_4), while the silicates again remain unaltered. To detect the presence of manganese in the particles of oxides revealed by the hydrogen treatment the previously treated sample is repolished and etched with a dilute solution of ferric chloride in alcohol: if the white metallic grains resulting from the hydrogen treatment are colored darker than the surrounding iron they contain some manganese. Finally to detect the presence of iron and manganese sulphide the polished sample is etched with a dilute solution of tartaric acid which colors sulphide of manganese lightly and iron sulphide decidedly.

Rosenhain considers it probable that the two distinct constituents of wrought-iron slag are two different silicates or, possibly, oxides of iron.

It is seen that writers generally ignore the presence of phosphoric acid in the slag from the puddling furnace, and still it generally contains from 3 to 5 per cent of it, and occasionally considerably more. If we assume that this phosphoric acid forms with iron a phosphate of the formula $3FeO.P_2O_5$, a simple calculation, according to atomic weights of the elements involved, will show that the presence of 5 per cent of phosphoric acid would mean the formation of over 12.50 per cent of this phosphate of iron. It is hardly to be supposed that this phosphate is absorbed by some other

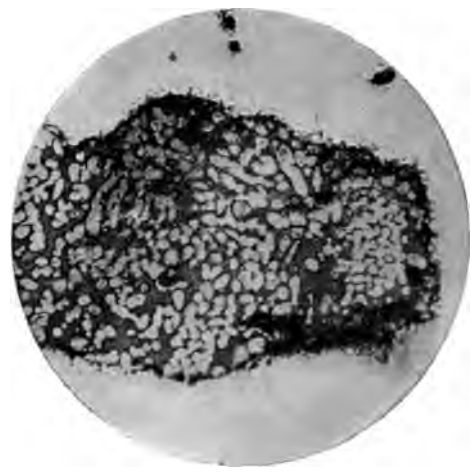


Fig. 5. — Particle of slag in wrought iron.
Magnified 200 diameters. (Guillet.)

constituent of the slag. On the contrary it seems highly probable that it must be present as a distinct constituent.

Influence of Thermal and Mechanical Treatments. — The dimensions of the ferrite grains of wrought iron are affected by the treatments, both thermal and mechanical, received by the metal. The effect of these treatments upon the structure of iron and steel will be considered in another lesson.

Experiments

A small piece of wrought-iron bar should be procured measuring preferably ½ in. square or round and ¾ in. long. This piece should be sawed in two *longitudinally*, conveniently with a hack-saw (preferably a power hack-saw), and one of the freshly cut surfaces prepared for microscopical examination.

The various methods which have been used or recommended for the polishing of iron and steel specimens preliminary to their microscopical examination will be found duly described in an appendix to these lessons. In connection with the experiments described in this book only those methods will be mentioned which in the author's opinion have been found most satisfactory.

Polishing by Hand. — The sharp edges of the sample should be filed or ground in order to avoid tearing the polishing cloths in the following operations. The sur-

face to be prepared should be filed first with a coarse and then with a smooth file so as to obtain a perfectly flat, smooth surface. This filing can be advantageously replaced by grinding on a fine emery-wheel. It is recommended that both filing or grinding be conducted with a very gentle pressure. In case the polishing is to be done by hand the hand polishing outfit described at the beginning of these lessons is recommended.

A small amount of No. 80 emery powder[1] mixed with sufficient water to form a thick paste should be placed on one of the polishing blocks covered with cotton cloth. This paste should be spread over the block, conveniently by means of a spatula, and with the addition of a little more water if necessary. The sample of metal should now be rubbed back and forth over this block, being careful to rub always in the same direction until the marks left by the file or emery-wheel have all been removed and replaced by finer markings due to the action of the emery powder. After this treatment the sample should be carefully washed, as well as the fingers of the operator, preferably in running water, and the sample rubbed over the second polishing block covered with cotton cloth and a little flour emery and water, precisely as before. On passing from the first to the second polishing block, the sample should be turned at right angles and kept in that position, in order that the new marks may be perpendicular to the old ones, and the polishing should be continued until the marks left by the coarse emery have been entirely effaced and replaced by finer ones. The sample after being carefully washed is ready for the next block. Some of the tripoli powder should be spread, with the addition of water, over one of the blocks covered with broadcloth, and the sample polished upon this block until the markings left by the previous polishing have been completely removed. After careful washing the sample should now be rubbed over the last polishing block, covered with broadcloth, rouge,[2] and water, holding as usual the sample so as to rub it at right angles to the markings left by the tripoli. After these markings have been removed the sample should have a very bright surface and be free from even microscopical scratches. At this stage a magnifying-glass is very useful for inspecting the specimen in order to ascertain whether it is ready for the etching treatment. For this purpose the vertical magnifier described and illustrated under "Apparatus" at the beginning of these lessons will be found very satisfactory.

On examining the polished sample of wrought iron with the naked eye many small, elongated cavities will be detected which will be more apparent still if viewed through a magnifying-glass. These marks correspond to the location of the slag fibers and will be readily distinguished from scratches.

The specimen should now be carefully washed and dried with a soft cloth, preferably a fine piece of old linen. Where an air-blast is at hand, as is generally the case in chemical laboratories, it is advisable to dry the specimen with this blast (a hot blast is more effective than a cold one) instead of rubbing it with a cloth. The sample may then be passed gently once or twice on a piece of chamois leather stretched over a smooth piece of wood and carefully protected from dust when not in use, when it will be ready for the next or etching operation. When polishing, the sample should be pressed lightly upon the blocks and great care taken not to carry any coarse powder over a polishing block upon which a finer powder is used as the presence of but a few coarser grains will greatly lengthen the operation. It is of

[1] The polishing powders should be of the very best quality obtainable.

[2] It is essential to use the best commercial grade of jeweler's rouge.

much importance, therefore, to keep all the blocks carefully covered when not in use as well as the bottles containing the powders.

Polishing by Power. — Polishing by hand is at best a tedious and laborious operation and whenever possible it is highly advisable to replace it by the use of a power polishing machine. Very satisfactory and effective polishing machines and polishing motors are illustrated and described in the introductory chapter on apparatus.

When using these polishing machines or polishing motors the manipulations are as follows:

The metal surface to be prepared is pressed lightly upon the emery-wheel until a perfectly flat surface is obtained, when it should be washed with the usual precautions and pressed upon the cloth-covered cast-iron disk placed next to the emery-wheel and upon which flour emery and water have been applied. Care should be taken to hold the specimen so that the new marks will cross the old ones at right angles and the grinding should be continued until the emery-wheel marks have been completely erased. After washing the specimen it is ready for treatment on the next surface covered with broadcloth upon which has been spread tripoli powder and water, here again turning the sample 90 degrees. When the marks left by the preceding operation have been removed, the specimen is washed and given the final polishing treatment by pressing it lightly upon the other side of the cast-iron disk upon which rouge and water is used. The various polishing powders mixed with water may be conveniently applied to their respective disks by means of flat and rather stiff brushes. The surface of a properly polished sample should be highly specular and free from scratches.

Time will be saved by exerting a slight pressure only while polishing, especially on the emery-wheel and emery disk, because deep marks due to these abrasers will be troublesome to remove with the finer powders. With these machines a sample of steel measuring ½ in. square or ½ in. in diameter is readily polished in 10 minutes.

Etching. — If the polished sample of wrought iron were now placed under the microscope, it would be possible to detect some of the slag particles but the structure of the iron itself could not be seen, because all parts of the sample being uniformly bright would reflect the light to the same extent. To make the structure apparent under the microscope it is necessary to impart unlike appearances to the constituents. This is generally accomplished by producing a slight corrosion or etching of the polished surface. For this purpose acid solutions are generally used which attack some constituents more deeply than others or to the exclusion of others, which action may or may not be accompanied by the deposition of some precipitated matter.

Arnold considers the operation of etching with dilute acids to be of an electrolytic nature, some of the constituents being electro-negative to others, hence the attack of some of these (electro-positive constituents) to the exclusion of others (electro-negative constituents) and the darker coloration of the former.

The various methods which have been used or recommended for the development of the structure of iron and steel samples will be found duly described in an appendix to these lessons but only those methods which in the author's opinion are most satisfactory will be mentioned in connection with the experiments of this book.

Etching with Picric Acid. (Igevsky.) — An etching solution should be prepared containing 5 grams of picric acid, chemically pure, and 95 cubic centimeters of absolute alcohol. This should be kept in a well-stopped glass bottle.

A small amount of this solution should be poured in a glass or porcelain dish, preferably a small crystallizing glass dish with cover, and the sample immersed in it for 30 seconds, when it should be removed, conveniently with a pair of pincers (preferably with platinum tips), and washed in alcohol. The sample should now be dried, preferably by means of a blast for which a foot-blower will answer very well. After rubbing the sample *very gently* once or twice upon a smooth piece of chamois leather stretched on a wooden block and carefully kept free from dust, it will be ready for examination.

Examination. — The prepared sample should be suspended to the magnetic specimen holder described under "Apparatus" in such a way as to expose to view as much as possible of its surface. The source of light and condensers should be adjusted so that a beam of light of suitable size enters the vertical illuminator; the light beam should cover a little more than the aperture of the illuminator. A 2 in. (X) eyepiece and a 16 mm. (⅔ in.) objective will be a satisfactory combination for the examination. The image of the specimen should be focussed roughly by the rack and pinion motion of the stage, and the milled head of the vertical illuminator turned tentatively and gently right and left until the sample appears brightly and uniformly lighted. The object should now be brought to a sharp focus by means of the fine adjustment.

The etching treatment should have outlined the joints between the ferrite grains clearly and sharply. If the structure lacks clearness it is safe to infer that the etching was not properly done. In that case the sample should be rubbed a few times on the chamois leather block and again examined without repeating the etching. If the structure remains ill-defined, rub the specimen a minute or two on the rouge block or disk, wash, dry, and repeat the etching treatment until satisfactory results are obtained.

Should the boundaries of the ferrite grains appear too faint, the etching treatment should be repeated without repolishing, so as to etch these lines more deeply.

As the usual purpose of the microscopical examination of samples of wrought iron is to ascertain the quantity and mode of occurrence of the slag and the dimensions of the ferrite grains, it is not generally desired to etch the sample so deeply that some of the grains become deeply colored, still less that etching pits begin to appear.

In this experiment, however, the student is advised to etch his sample gradually so that the different stages of the structure may be clearly seen: — (1) before etching: slag fibers and a brilliant structureless matrix, (2) after a slight etching: ferrite grains sharply defined but remaining uncolored or but slightly colored, (3) after a deeper etching: some of the ferrite grains deeply colored, and (4) after a still deeper etching: small cubic etching pits beginning to appear.

The production of these etching pits, however, is often a troublesome and uncertain operation. Heyn recommends for that purpose etching with double chloride of copper and ammonium, others (Stead) "a sufficiently long immersion in lukewarm 20 per cent sulphuric acid, followed by cleaning in nitric acid."

Etching with Diluted Nitric Acid. — The sample used in the above experiment should be rubbed a short while on the rouge block so as to remove the effect of the etching, washed and dried in the usual way and etched with a solution containing 10 c.c. of concentrated, chemically pure nitric acid and 90 c.c. of absolute alcohol. The etching should be conducted in the same way but as this reagent acts more

quickly the sample should not be left in the solution more than 10 or 15 seconds, when it should be washed in alcohol, carefully dried and passed gently once or twice over the chamois leather block.

If the boundaries of the grains are too faintly developed the etching should be repeated without repolishing.

The appearance of the sample after this treatment should be identical to that resulting from etching with picric acid, the only essential difference between these two reagents being the slower action of the latter.

Etching with Concentrated Nitric Acid. (Sauveur.) — The corrosion due to the last treatment should be removed by rubbing the sample on the rouge block which after careful washing and drying should now be etched with concentrated nitric acid as follows: The polished specimen conveniently held with a pair of pincers (preferably with platinum tips) should be dipped in a beaker or other vessel containing concentrated nitric acid (1.42 specific gravity) and immediately afterwards held under an abundant stream of running water. When iron is immersed in concentrated nitric it assumes the passive state, that is, it is not affected by the acid. As soon, however, as the layer of concentrated acid which covers the polished surface is diluted by the running water, the steel is vigorously attacked but for so short a time (since the water soon removes all traces of acid) that there is little danger of etching too deeply. One such treatment is generally sufficient to bring out the structure sharply and clearly but if the specimen is found insufficiently etched, the etching should be repeated in exactly the same manner. The author believes that the simplicity of this etching treatment and the excellent results generally obtained have been overlooked by metallographists.

Transverse Section of Wrought-Iron Bar. — The student should prepare a transverse section (preferably not over ½ in. thick) of the same wrought-iron bar, following exactly the manipulations described for the polishing and etching of the longitudinal section. He should compare the structure of the two sections and notice (1) their similarity as to the appearance of the ferrite grains and (2) the unlike occurrence of the slag which in the transverse section is present as small irregular areas corresponding to cross sections of the slag fibers of the longitudinal section.

Examination

I. Describe briefly the structure of commercial wrought iron, explaining the difference between the appearances of longitudinal and transverse sections.

II. Describe the structure of your samples and mention any difficulty which you may have encountered in your manipulations.

III. If you have any preference for one of the etching methods described give your reasons in support of it.

LESSON IV

LOW CARBON STEEL

In this and the following lessons steel will be considered as a pure alloy of iron and carbon, i.e free from the impurities (silicon, manganese, sulphur, and phosphorus) always present in commercial products. The influence of these elements upon the structure of steel will form the subject of another lesson.

Normal Structure. — The structures described in this and the next lesson refer to the condition of steel after forging followed by heating to, and slowly cooling from, a high temperature (900 to 1000 deg. C.). Such treatments, for reasons that will be understood later, promote soundness, remove internal strains, prevent excessive coarseness of structure (as in castings), and permit a state of stable equilibrium to be assumed by the constituents. The resulting structure may be conveniently called the "normal" structure and it will be so called in these lessons.

Grading of Steel vs. Carbon Content. — Steel is generally graded according to the amount of carbon it contains. The following terms are those most commonly used:

Very low carbon steel, very mild or extra mild steel, very soft or dead soft steel	carbon not over 0.10 per cent
Low carbon steel, mild steel, soft steel	carbon not over 0.25 per cent
Medium high carbon steel, half hard steel	carbon 0.26 to 0.60 per cent
High carbon steel, hard steel	carbon over 0.60 per cent
Very high carbon steel, very hard or extra hard steel	carbon over 1.25 per cent

This classification is somewhat arbitrary as there are no sharp lines of demarcations universally recognized between the various grades.

It will be seen in another lesson that steel containing about 0.85 per cent carbon is also known as eutectoid steel, steel containing less carbon as hypo-eutectoid steel and more highly carburized metal as hyper-eutectoid steel.

Low Carbon Steel vs. Wrought Iron. — As already mentioned the distinction between low carbon steel and wrought iron is based upon the difference between the methods employed for their respective manufacture rather than upon unlike chemical or physical properties, for these metals may indeed be quite identical both physically and chemically. The mere melting of wrought iron would undoubtedly, in accordance with the universally accepted definition of steel, convert it into steel since we would now have a malleable metal *initially cast*. Such treatment would of course result in the elimination of the slag mechanically retained by the wrought iron: the melted metal would be slagless, barring cemented steel, another essential property of steel. Since wrought iron generally contains but a small amount of carbon, melting it would convert it into low carbon steel.

The Structure of Low Carbon Steel. — From the above considerations regarding the resemblance between wrought iron and low carbon steel, the structure of the latter may fairly be anticipated. Seeing that low carbon steel may be considered as wrought iron from which the mechanically held slag has been expelled through melt-

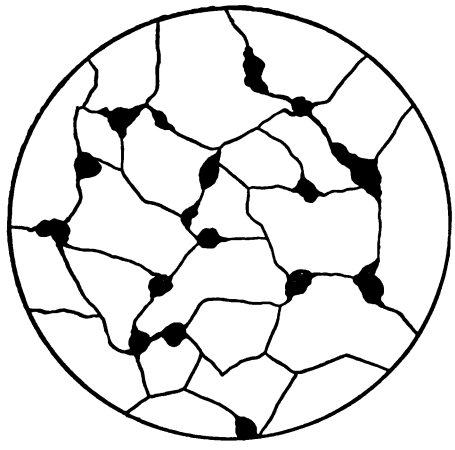


Fig. 1. — Steel. Carbon 0.08 per cent. Magnification not stated. (Arnold.)

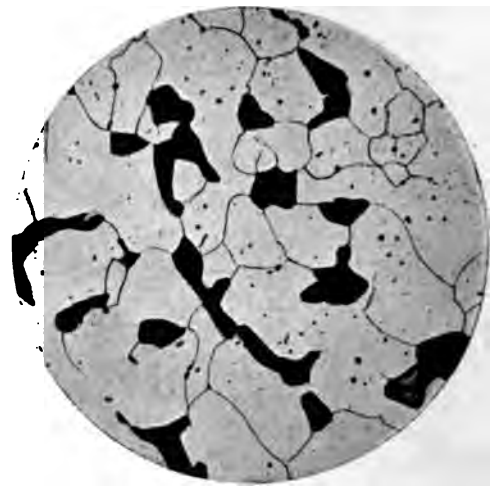


Fig. 2. — Steel. Carbon about 0.20 per cent. Magnified 200 diameters. (Guillet.)

ing, we should expect the absence of slag to be the only marked difference between the structure of low carbon steel and that of wrought iron.

The microstructure of low carbon steel in the case of samples containing respectively about 0.10 and 0.20 per cent carbon is illustrated in Figures 1 to 5. It will be

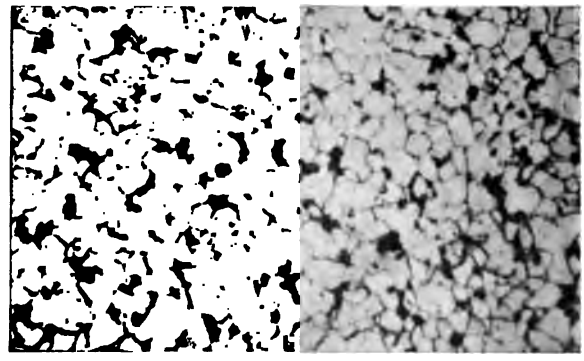


Fig. 3. — Steel. Carbon 0.10 per cent. Magnified 100 diameters. (Boynton.)

seen (Figs. 1, 2, and 3) to consist chiefly of a mass of ferrite (carbonless iron) exhibiting the usual polyhedral crystalline grains described in preceding lessons. The ferrite present in low carbon steel is similar in every respect to the ferrite of wrought iron. At the junctions of many ferrite grains, however, some dark areas will be noted, an evi-

dence of the existence in the metal of another constituent. Since ferrite is practically free from carbon, it is evident that the carbon present in the steel must have segregated into these small dark masses. As to the exact nature of this dark constituent it will be apparent that it cannot consist of pure carbon for it is well known that the carbon present in steel does not exist in the free state but on the contrary is combined with some of the iron forming a definite chemical compound or carbide of iron whose formula is Fe_3C.[1] This iron carbide must necessarily be located in the dark areas, but are these made up exclusively of this carbide? To find an answer to this question let us examine the structure of steel under a higher magnification (Figs. 4 and 5). This reveals the existence of two components in each dark particle occurring as small wavy or curved parallel plates or lamellæ alternately dark and white. As to the nature of these two components, it is evident that one of them must be the carbide Fe_3C and the other necessarily iron or ferrite, since according to the proximate analysis of steel, these are the only two constituents which, to the best of our knowledge, are present in pure unhardened carbon steel.

Pearlite. — Howe named the microscopical constituent just described pearlite (originally written pearlyte) following in this Dr. Sorby who was the first observer to describe it and who had proposed for it the name of "pearly constituent" because it frequently exhibits a display of colors very suggestive of mother-of-pearl, especially when viewed by oblique illumination. This appearance is due to the fact that these plates are extremely thin, seldom measuring over $\frac{1}{25000}$ of an inch in thickness, and that the plates of carbide, being much harder than the ferrite plates, stand in relief after polishing, resulting in an arrangement very similar to the refraction gratings of physicists. Mother-of-pearl likewise is made up of very thin alternate plates of different colors and possibly of different hardness. The carbide plates remain bright not being affected by the usual etching reagents, while the ferrite plates appear dark because of their being somewhat tarnished by the etching and also because, being depressed owing to their greater softness, they stand in the shadow of the carbide plates. It will be shown in another lesson that in many series of alloys of two metals the alloy of lowest melting-point called the "eutectic" alloy, nearly always exhibits a composite structure like that of pearlite, i.e. made up of parallel plates alternately of one and the other constituents. It will also be shown that in spite of this very great structural resemblance pearlite is not a true eutectic alloy. Howe proposed to call "eutectoid" the kind of mechanical mixture found in pearlite and this most appropriate term has been universally adopted.

Because of the minute dimensions of the lamellæ of pearlite a high magnification, generally not less than 250 or 300 diameters, is required for its resolution.

It should be stated here that pearlite does not always assume such a distinctly laminated structure. In many instances its structure remains ill defined or has a granular rather than a lamellar appearance, while its behavior towards the etching reagents likewise varies. It will be shown at the proper time that this is due to the treatments to which steel may be subjected and that the exact nature of these ill-defined forms of pearlite (often called transition constituents) has given rise to a large amount of discussion and has been the object of many investigations. It may be

[1] The existence of the carbide Fe_3C in unhardened steel was first shown in 1885 by Abel and Muller, working independently, and has since been confirmed by many other investigators. Its existence is proved by dissolving unhardened steel in a suitable solvent and analyzing the carbonaceous residue.

assumed for the present that any pearlite which is not distinctly lamellar is not true pearlite.

It will be noted that in Figure 2 the pearlite occupies about twice the area covered by the same constituent in Figure 1. We infer from this that the amount of pearlite in low carbon steel at least increases progressively with the carbon content. Doubling the amount of carbon doubles of course the proportion of the iron carbide in the steel, and since the amount of pearlite is apparently also doubled it follows that iron carbide and ferrite must unite with each other in fixed ratio to form pearlite, in other words that pearlite always contains the same proportion of carbide and hence also of carbon. The accuracy of this conclusion will soon be shown.

Free Ferrite. — To distinguish between the ferrite included in pearlite and the ferrite forming the balance of low carbon steel, the latter is sometimes called "free"

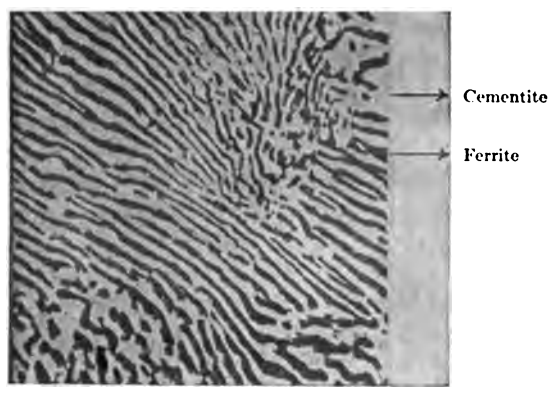


Fig. 4. — Steel. Structure of pearlite. Magnified 1000 diameters. (Osmond.)

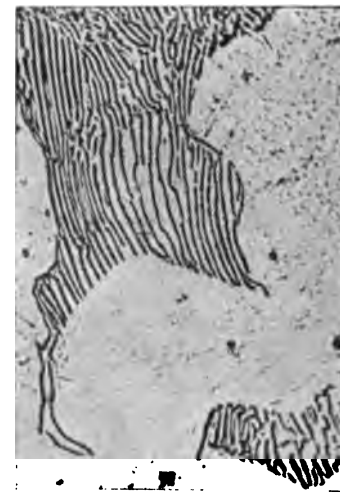


Fig. 5. — Steel. Hypo-eutectoid. Magnified 750 diameters. Pearlite particles and surrounding ferrite. (Goerens.)

ferrite, "structurally free" ferrite, "excess" ferrite, "massive" ferrite, "non-eutectoid" or "pro-eutectoid" ferrite, "surplus" ferrite. In these lessons it will be referred to as free ferrite while the ferrite forming part of the pearlite will be called pearlite-ferrite. Some writers refer to the latter as eutectoid-ferrite.

In the absence of any conclusive evidence to the contrary, it is natural to infer that free ferrite and pearlite-ferrite are identical, that is, pure iron in pure steel and iron holding in solution small quantities of silicon and phosphorus, and possibly of other impurities, in impure (commercial) steel.

This has been doubted by some writers, however, who have noted that the ferrite of some pearlites was more readily colored on etching than free ferrite and they saw in this and in some other evidences an indication that pearlite-ferrite may be less pure than free ferrite. Benedicks, for instance, believes, or at least believed at one time, that the pearlite-ferrite of some steels could contain as much as 0.27 per cent of carbon dissolved in beta iron, whereas free ferrite is in the alpha condition. This carburized and allotropic ferrite Benedicks called "ferronite."

Cementite. — The name of cementite has been given by Howe to the carbide Fe_3C and universally adopted. The term is derived from "cement" steel (cementation steel, blister steel, converted steel) which being generally a high carbon steel contains a great deal of this carbide, that is, of cementite.

According to the atomic weights of iron (56) and of carbon (12) cementite must contain

$$\frac{12 \times 100}{3 \times 56 + 12} = 6.67 \text{ per cent carbon}$$

The carbon present in cementite is frequently referred to as "cement" carbon, occasionally as carbide carbon, to distinguish it from other forms of carbon found in iron and steel and to be described later (hardening carbon, graphitic carbon, temper carbon, etc.).

Cementite is an extremely hard substance, being in fact the hardest of all the constituents occurring in iron and steel, harder even than hardened, high carbon steel. Howe states that it is harder than glass and nearly as brittle. As it scratches feldspar but not quartz it is generally assigned to rank 6 or 6.5 in the Mohs scale of hardness.[1]

It will be shown later that when steel contains an appreciable amount of manganese, as is nearly always the case in commercial products, a portion at least of this manganese also forms an iron carbide Mn_3C and that this carbide unites with the iron carbide Fe_3C to form cementite. It is well to bear in mind, therefore, that in commercial steel cementite generally contains besides Fe_3C varying amounts of this carbide of manganese. As the atomic weight of manganese is nearly the same as that of iron, 55 compared to 56, it so happens that the presence of manganese in cementite affects but very little its carbon content, which for all practical purposes may be taken as 6.67 regardless of the amount of manganese it may contain. Cementite containing much manganese has been called manganiferous cementite by some writers.

Whether any portion of the other impurities present in iron and steel (sulphur, silicon, phosphorus) is ever included in cementite is not positively known but in the absence of indications to the contrary it is generally assumed that cementite is free, practically at least, from these metalloids.

Cementite generally remains bright and brilliant after the ordinary etching treatments employed to reveal the structure of steel. It will be shown later, however, that some special reagents may be used which color it deeply.

Experiments

The student should procure samples of forged steel containing respectively about 0.10 and 0.20 per cent carbon. These should be heated to 1000 deg. C. and slowly cooled, preferably with the furnace in which they were heated.

Polishing. — Specimens should be cut from these samples of suitable size for microscopical examinations (preferably not over 1½ in. square or round and ½ in. thick). These specimens should be polished for examination in accordance with the instruction given in Lesson III, taking care to prepare a freshly cut surface, that is a portion of the sample which did not suffer from decarburization in the furnace.

[1] The Mohs scale is as follows, beginning with the softest and ending with the hardest mineral and each mineral being capable of scratching the preceding ones: (1) Talc, (2) Gypsum, (3) Calcite, (4) Fluorite, (5) Apatite, (6) Feldspar, (7) Quartz, (8) Topaz, (9) Corundum, and (10) Diamond.

chromatic aberration is never perfect, it is evident that the use of monochromatic light, i.e. light of one wave length, is theoretically preferable, especially for photographing.

Monochromatic light may be obtained in two ways: (*a*) by using a source of light actually monochromatic and (*b*) by causing white light to pass through colored glass screens or colored solutions (light filters), preventing the passage of some undesirable rays. The mercury arc lamp yields a nearly monochromatic light and has been tried by Le Chatelier with satisfactory results. It seems more convenient, however, when monochromatic light is wanted, to use light filters of suitable colors, in which case colored glass screens will be found easier to manipulate than glass cells containing colored solutions.

The beginner is advised to dispense with the use of colored screens or other ray filters until he has acquired experience and skill in taking photomicrographs, when he will be better qualified to judge of their merits and to employ them intelligently.

Photographic Plates. — The use of so-called "Process" or "Contrast" plates is recommended. These plates are slow but generally yield negatives with sharp contrasts. Orthochromatic plates may also be used with, in some instances, excellent results. These plates are much more rapid but as they call for the use of a colored screen, the time of exposure may be even longer than with the slower kind.

Development. — Formula and directions accompany each box of plates and the student could not do better than to follow them faithfully.

Printing. — Any printing out or developing paper may be used, the printing, developing, or toning being conducted in the usual way. Drying on ferrotype plates affords a quick means of finishing the prints and giving them a satisfactory luster. It is recommended to trim the prints round, 2 to 2½ inches in diameter, by means of a margin trimmer and suitable circular forms, as this will give them a very neat appearance.

Mounting. — It is well to paste the prints on suitable cardboard mounts affording room for the recording of useful data. A very satisfactory mount has been illustrated under "Apparatus."

Examination

I. Describe the structure of low carbon steel and more especially of pearlite.

II. What is free ferrite?

III. Describe the structure of your samples and mention any difficulty encountered in polishing, etching, or photographing them.

LESSON V

MEDIUM HIGH AND HIGH CARBON STEEL

Medium High Carbon Steel. — The normal structure of steel (i.e. its structure after forging, reheating to a high temperature and slow cooling) containing about 0.30 per cent carbon is illustrated by a drawing in Figure 1 and by a photomicrograph in Figure 2. It will be noted, on comparing this structure to that of lower carbon steels (Lesson IV), that the introduction of more carbon in the iron has resulted, as would be expected, in the occurrence of a greater amount of pearlite and of a correspondingly smaller proportion of ferrite. The pearlite occupies now roughly about one third of the total area. The junction lines between the grains of ferrite

Fig. 1. — Steel. Carbon 0.38 per cent. Magnification not stated. (Arnold.)

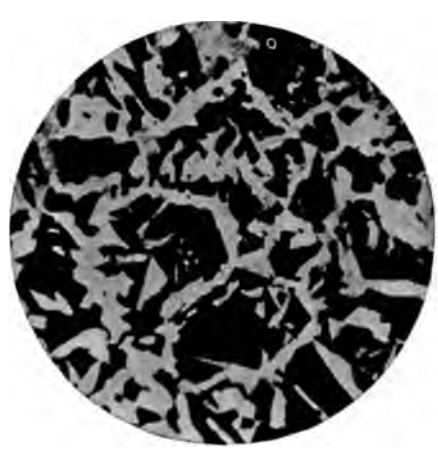


Fig. 2. — Steel. Carbon 0.33 per cent. Magnified 100 diameters. Heated to 1000 deg. C. and slowly cooled in furnace. (Hall.)

should be noted. Under sufficiently high power the pearlite areas exhibit the characteristic lamellar structure described in Lesson IV.

On further addition of carbon, the amount of pearlite, which is evidently proportional to the percentage of carbon, increases correspondingly, as shown in Figures 3 and 4 illustrating the microstructure of steel containing about 0.50 per cent carbon. The pearlite occupies here over one half of the total area. It will be noticed that the ferrite areas are only occasionally resolved into polyhedral grains, apparently because the ferrite now occurs in particles often too small to be made up of several crystalline grains. These small masses of ferrite, however, are still made up of crystalline matter as described and illustrated in Lesson II. A high power photomicro-

graph of 0.45 per cent carbon steel is shown in Figure 5. The laminations of pearlite are clearly seen.

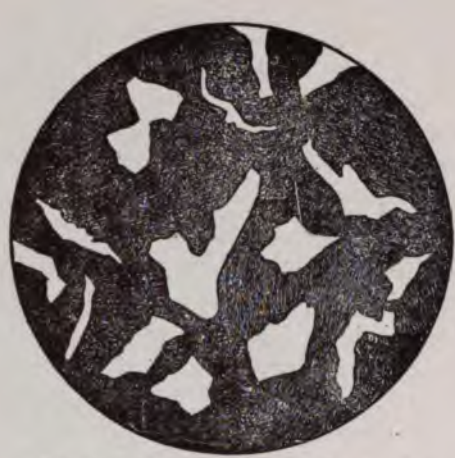


Fig. 3. — Steel. Carbon 0.59 per cent. Magnification not stated. (Arnold.)

Fig. 4. — Steel. Carbon 0.50 per cent. Magnified 100 diameters. Heated to 1000 deg. C. and slowly cooled in furnace. (Burger.)

Fig. 5. — Steel. Carbon 0.45 per cent. Magnified 1000 diameters. (Osmond.)

When steel contains but a small, although appreciable, amount of ferrite, as is the case with carbon contents between 0.50 and 0.70 per cent the ferrite frequently forms envelopes or membranes surrounding the pearlite grains, an arrangement

generally described as a network structure the pearlite forming the meshes and the free ferrite the net proper. These pearlite meshes are also described as "cells" or "kernels" and the ferrite membranes as "cell walls" or "shells."

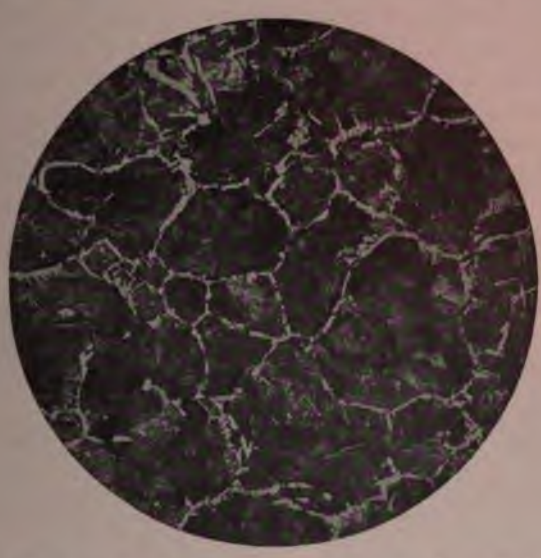


Fig. 6. — Steel. Carbon 0.50 per cent. Magnified 100 diameters. Heated to 1000 deg. C. and cooled in air. (Burger.)

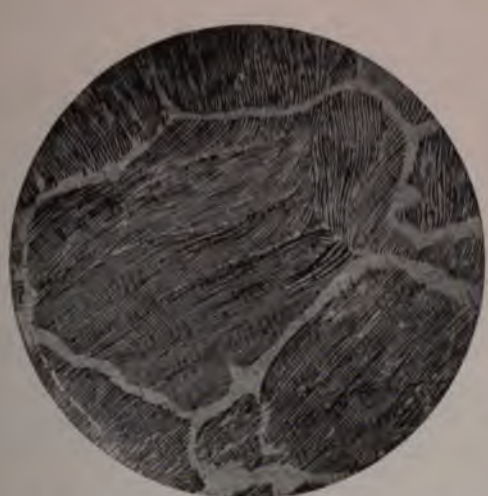


Fig. 7. — Steel. Hypo-eutectoid. (Sorby.)

It will be shown later that this network structure is promoted by rather rapid cooling from a high temperature, as for instance by cooling small pieces in air.

Structures of this type are illustrated in Figures 6 and 7. The latter illustration is of special interest being a reproduction of one of Sorby's original drawings and therefore, the first drawing of pearlite ever published.

High Carbon Steel. — Since the introduction of increasing amounts of carbon in steel results in the formation of a correspondingly increasing proportion of pearlite and decreasing proportion of ferrite, a degree of carburization must necessarily be reached, when the whole mass will be made up of pearlite, the ferrite having finally disappeared. This critical point in the structure of steel is attained when the metal contains somewhere between 0.80 and 0.90 per cent of carbon, exceptionally pure steel requiring the larger proportion of carbon and impure steel the smaller for the complete disappearance of ferrite.

Eutectoid Steel. — Steel made up exclusively of pearlite is now quite universally called "eutectoid" steel, after Howe, the name suggesting the great resemblance between pearlite and euctectic alloys, while, at the same time, clearly indicating that pearlite is not a real eutectic alloy. Previous to Howe's happy suggestion

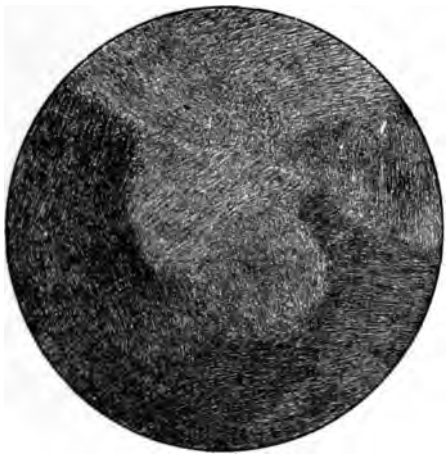


Fig. 8. — Steel. Carbon 0.89 per cent. Magnification not stated. (Arnold.)

Fig. 9. — Steel. Eutectoid. Magnified 750 diameters. (Goerens.)

this steel was commonly described as "eutectic" or "saturated" steel. It has also been termed "aeolic" or "benmutic" steel but these names have now been abandoned. The structure of eutectoid steel is illustrated in Figures 8 and 9.

Steel containing less than 0.85 per cent carbon or thereabout, and in which, therefore, some free ferrite is present, is called "hypo-eutectoid," while steel more highly carburized than eutectoid steel is called "hyper-eutectoid." It will be shown presently that hyper-eutectoid steel contains free cementite.

Hyper-Eutectoid Steel. — The normal structure of steel containing from 1.10 to 1.50 per cent carbon is illustrated in Figures 10 to 13 both under low and high magnification. These steels will be seen to consist, like hypo-eutectoid steel, of two constituents, one of which being pearlite as clearly shown when examined under high power. The other constituent remains bright after etching and might at first be taken for ferrite. Upon reflection, however, it will be evident that such cannot be its nature. The light constituent of hyper-eutectoid steel consists of cementite which is now present in excess over the amount required to form pearlite, just as in hypo-

[illegible] steel, ferrite is the excess constituent. It will be evident that the ferrite and cementite which constitute all grades of carbon steels combine with each other in definite proportions to form pearlite, leaving, as the case may be, an excess of

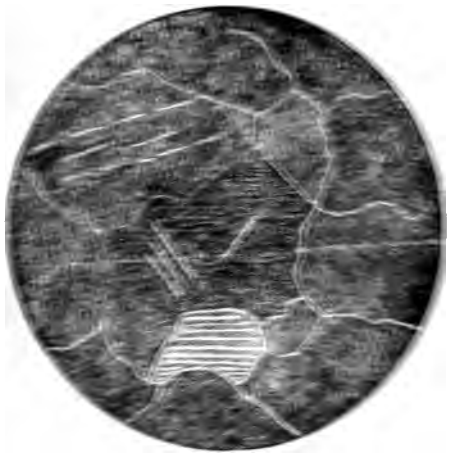


Fig. 10. — Steel. Carbon 1.20 per cent.
Magnification 100 diameters. Etched.

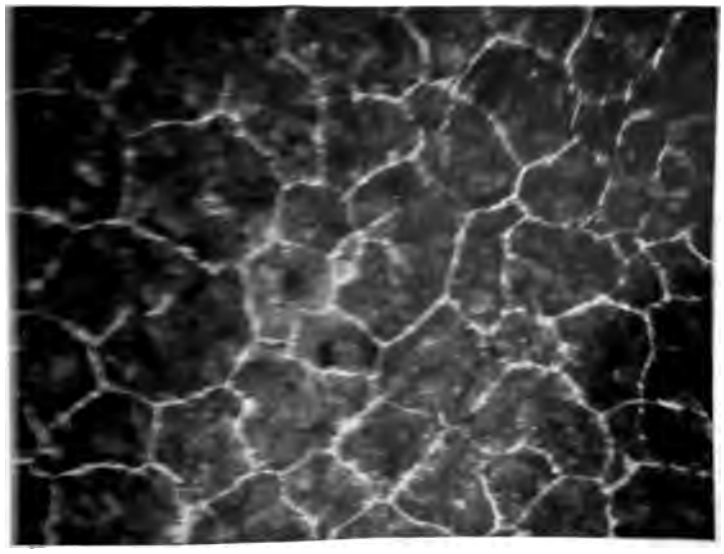


Fig. 11. — [illegible] Magnified 100 diameters. Etched.

[illegible] in hypo-eutectoid steel or [illegible] of cementite in hyper-eutectoid steel). A [illegible] scientific explanation [illegible] formation of the normal structure of steel will be [illegible] a subsequent lesson.

Free Cementite. To distinguish between the cementite forming part [illegible] pearlite (the bright areas of that constituent) and the cementite constituting

Carbon Content of Pearlite. — The percentage of carbon in pearlite, and, therefore, in eutectoid steel, has been stated to be somewhere between 0.80 and 0.90 in commercial steel of ordinary quality, because when steel of that degree of carburization is examined under the microscope it is found to be free from any appreciable amount of free ferrite or of free cementite. As the presence of a very small amount of any of these two constituents in the free state, however, is very difficult to ascertain, it will be evident that it is quite impossible to speak positively as to the exact amount of carbon needed to exclude both free ferrite and free cementite from the structure. Moreover this carbon content of pearlite varies somewhat with the com-

Fig. 14. — Steel. Hyper-eutectoid. Free cementite colored dark by sodium picrate. Magnified 500 diameters. (Guillet.)

Fig. 15. — Steel. Hyper-eutectoid. Free cementite colored dark by ammonium oxalate. Magnified 142 diameters. (Matweieff.)

position of the steel and with the treatment it has received. In steel of ordinary commercial purity the eutectoid point appears to be in the vicinity of 0.85 per cent carbon.

Structural Composition of Steel. — Bearing in mind that hypo-eutectoid steel is composed of free ferrite and pearlite and that hyper-eutectoid steel consists of free cementite and pearlite, and knowing the proportion of carbon in pearlite (0.85 per cent?) and in cementite (6.67 per cent), the structural composition of any steel may be readily calculated, provided we know the percentage of carbon it contains.

In case of hypo-eutectoid steel we have the two following equations:

$$(1)\quad F + P = 100$$

$$(2)\quad \frac{E}{100} P = C$$

in which F represents the percentage of free ferrite in the steel, P the percentage of pearlite, E the percentage of carbon in pearlite, and C the percentage of carbon in the steel. The first equation expresses the fact that the steel is composed of ferrite and pearlite and the second equation the fact that all the carbon in the steel is in-

cluded in the pearlite. Assuming, for instance, that pearlite contains 0.85 per cent carbon and the steel 0.50 per cent carbon, the resolution of these two equations indicates that steel of that grade has the following structural composition:

$$F = \text{per cent free ferrite} = 41.8$$
$$P = \text{per cent pearlite} = 58.2$$

In case of hyper-eutectoid steel the following two equations may be written:

$$(1)\quad P + Cm = 100$$
$$(2)\quad \frac{E}{100} P + \frac{6.67}{100} Cm = C$$

in which P represents the percentage of pearlite, Cm the percentage of free cementite, E the percentage of carbon in pearlite, C the percentage of carbon in the steel. The first equation expresses the fact that hyper-eutectoid steel is composed of pearlite and free cementite and the second the fact that the carbon in the steel is distributed between the pearlite and the free cementite, forming E per cent of the pearlite and 6.67 per cent of the cementite. Assuming the value of E to be 0.85 and the steel to contain 1.25 per cent carbon, these equations give for a steel of that grade

$$P = \text{per cent pearlite} = 93$$
$$Cm = \text{per cent free cementite} = 7$$

Supposing that pearlite or eutectoid steel contains 0.85 per cent carbon, since the whole of that carbon is present in the cementite plates of pearlite and since cementite contains 6.67 per cent carbon (as called for by its chemical formula Fe_3C), the percentage of cementite in pearlite may be readily calculated, as follows:

$$\frac{6.67}{100} \times \text{per cent cementite} = 0.85$$
$$\text{hence, per cent cementite} = 0.85 \times \frac{100}{6.67} = 12.74$$
$$\text{and per cent ferrite} = 100 - 12.74 = 87.26$$

or roughly 1 part by weight of cementite to 6.6 parts by weight of ferrite.

If it be considered, however, (1) that the exact carbon content of pearlite is not, and, hardly can be, known, (2) that it varies somewhat both with composition and treatment, and (3) that in commercial steel it is probably not far from 0.85 per cent, we are fully warranted to assume, for the sake of the great simplicity it introduces in the calculations, that pearlite contains exactly 1 part by weight of cementite to 7 parts by weight of ferrite, which would be the case if the eutectoid point corresponded to 0.834 per cent carbon, as indicated below:

1 part cementite + 7 parts ferrite yields 8 parts pearlite
or 12.50 per cent cementite + 87.50 per cent ferrite = 100 per cent pearlite

and since cementite contains 6.67 per cent carbon, 12.50 per cent cementite will contain $6.67 \times .1250 = 0.834$ per cent carbon. Assuming then that such is the carbon content of eutectoid steel, so that 1 part of cementite gives exactly 8 parts by weight of pearlite and, noting that the carbon in the steel produces exactly 15 times its own

weight of cementite,[1] the calculation of the structural composition of any steel becomes extremely simple.

In case of hypo-eutectoid steel (steel containing less than 0.834 per cent carbon) we have

per cent total cementite = per cent total carbon × 15
and per cent pearlite = per cent total cementite × 8

or, more simply,

per cent pearlite = per cent carbon × 120
i.e. P = 120 C

and, of course, per cent ferrite = F = 100 − P.

With hyper-eutectoid steel (steel containing more than 0.834 per cent carbon) the figuring is as follows:

Since 8 parts of pearlite contains 7 parts of ferrite and since in hyper-eutectoid steel the totality of the ferrite (total ferrite) is included in the pearlite (there being no free ferrite) we have

per cent pearlite = P = $\frac{8}{7}$ total ferrite
or, since total ferrite = 100 − total cementite,
P = $\frac{8}{7}$ (100 − total cementite)

But total cementite = carbon × 15, hence

$$P = \frac{8}{7}(100 - 15\,C)$$

$$\text{or } P = \frac{800 - 120\,C}{7}$$

and, of course, free cementite = Cm = 100 − P.

Summing up, in order to find the percentage of pearlite in hypo-eutectoid steel it will suffice to multiply its carbon content by 120 (P = 120 C), the balance of the steel, consisting, of course, of free ferrite (F = 100 − P); to find the percentage of pearlite in hyper-eutectoid steel, the percentage of carbon in the steel should be substituted for C in the formula: $P = \frac{800 - 120\,C}{7}$ and the balance of the steel will be made up of free cementite (Cm = 100 − P).

Taking, for instance, a steel containing 0.50 per cent carbon. Its structural composition will be:

120 × 0.50 = 60 per cent pearlite, and
100 − 60 = 40 per cent ferrite

If a steel contains 1.25 per cent carbon the resulting percentage of pearlite will be $\frac{800 - 120 \times 1.25}{7}$ or nearly 93 per cent and the free cementite (Cm), 100 − 93 = 7 per cent.

[1] This follows from the composition of Fe_3C indicated by the atomic weights of iron and carbon:

(3 × 56) Iron + 12 Carbon = 180 Fe_3C

hence one part carbon produces $\frac{180}{12} = 15$ parts Fe_3C or cementite.

In these lessons it will be assumed for the sake of the simplicity it introduces that pearlite contains 0.834 per cent carbon, that is exactly 1 part by weight of cementite to 7 parts of ferrite.

Chemical vs. Structural Composition. — Disregarding for the present the existence of impurities, the ultimate analysis of steel reveals the presence of so much carbon and so much iron. The proximate chemical analysis of steel reveals (in steel slowly cooled from a high temperature) the presence of so much iron and so much carbide of iron, Fe_3C. In a similar way we may consider two different structural compositions, an ultimate and a proximate one. The ultimate structural composition reveals the presence of so much total ferrite and so much total cementite, while the proximate structural composition informs us of the percentages of pearlite, free ferrite, and free cementite in the steel. It will be evident that the chemical proximate composition is identical to the ultimate structural composition, the names of the constituents only being different, iron and carbide in the first case, ferrite and cementite in the latter.

These various compositions are tabulated below:

		Constituents		
Chemical Composition	ultimate	Fe	C	
	proximate	Fe	Fe_3C	
Structural Composition	ultimate	total ferrite	total cementite	
	proximate	pearlite	free ferrite	free cementite

It is apparent that the proximate structural composition affords more valuable information than is obtainable through the other three kinds of analysis, for not only does it indicate the chemical nature of the proximate constituents but also their structural association and occurrence, upon which depend, to a very great extent, the physical properties of steel. In the following table (page 12) the ultimate chemical composition as well as the structural composition, both ultimate and proximate, of steel containing from 0.1 to 2.0 per cent of carbon, have been calculated for each increase of carbon of 0.1 per cent. Corrections for variations of 0.01 per cent carbon can readily be obtained by interpolation and are indicated in a second table. The values given for the proximate compositions are based upon the assumption that pearlite contains 0.834 per cent carbon.

These compositions are shown also diagrammatically in Figure 16 which will be readily understood. ABC represents the free ferrite in hypo-eutectoid steel, ACD the pearlite in hypo-eutectoid steel, DCEF the pearlite in hyper-eutectoid steel, DFG the free cementite in hyper-eutectoid steel, ABEH the total ferrite in any steel, AHG the total cementite in any steel, ACEH the pearlite-ferrite in any steel, and AHFD the pearlite-cementite in any steel.

CHEMICAL COMPOSITION		STRUCTURAL COMPOSITION				
Ultimate		Ultimate		Proximate		
C	Fe	Total Cementite	Total Ferrite	Pearlite	Free Ferrite	Free Cementite
.1	99.9	1.5	98.5	12.0	88.0	—
.2	99.8	3.0	97.0	24.0	76.0	—
.3	99.7	4.5	95.5	36.0	64.0	—
.4	99.6	6.0	94.0	48.0	52.0	—
.5	99.5	7.5	92.5	60.0	40.0	—
.6	99.4	9.0	91.0	72.0	28.0	—
.7	99.3	10.5	89.5	84.0	16.0	—
.8	99.2	12.0	88.0	96.0	4.0	—
.9	99.1	13.5	86.5	98.7	—	1.3
1.0	99.0	15.0	85.0	97.0	—	3.0
1.1	98.9	16.5	83.5	95.3	—	4.7
1.2	98.8	18.0	82.0	93.6	—	6.4
1.3	98.7	19.5	80.5	91.9	—	8.1
1.4	98.6	21.0	79.0	90.2	—	9.8
1.5	98.5	22.5	77.5	88.5	—	11.5
1.6	98.4	24.0	76.0	86.8	—	13.2
1.7	98.3	25.5	74.5	85.1	—	14.9
1.8	98.2	27.0	73.0	83.4	—	16.6
1.9	98.1	28.5	71.5	81.7	—	18.3
2.0	98.0	30.0	70.0	80.0	—	20.0

Carbon	Hypo-Eutectoid Steel	Hyper-Eutectoid Steel
%	Values to be added to % of pearlite and subtracted from % cementite	Values to be subtracted from % pearlite and added to % cementite
0.01	1.2	0.17
0.02	2.4	0.34
0.03	3.6	0.51
0.04	4.8	0.68
0.05	6.0	0.85
0.06	7.2	1.02
0.07	8.4	1.19
0.08	9.6	1.36
0.09	10.8	1.53

Micro-Test for Determination of Carbon in Steel. — Since the amount of pearlite in steel is proportional to the percentage of carbon it contains, it should be possible to estimate the latter with a fair degree of accuracy from the area occupied by the pearlite. After a little experience and by taking the necessary precautions it will be found that, in the case of decidedly hypo-eutectoid steels at least (steels containing say less than 0.60 per cent carbon), results are obtained fully as accurate as those of the colorimetric method and, on the whole, more reliable, since the possibility of serious errors is practically eliminated. By the micro-test, for instance, a steel with 0.25 per cent carbon might be reported as containing 0.20 or 0.30 per cent of that

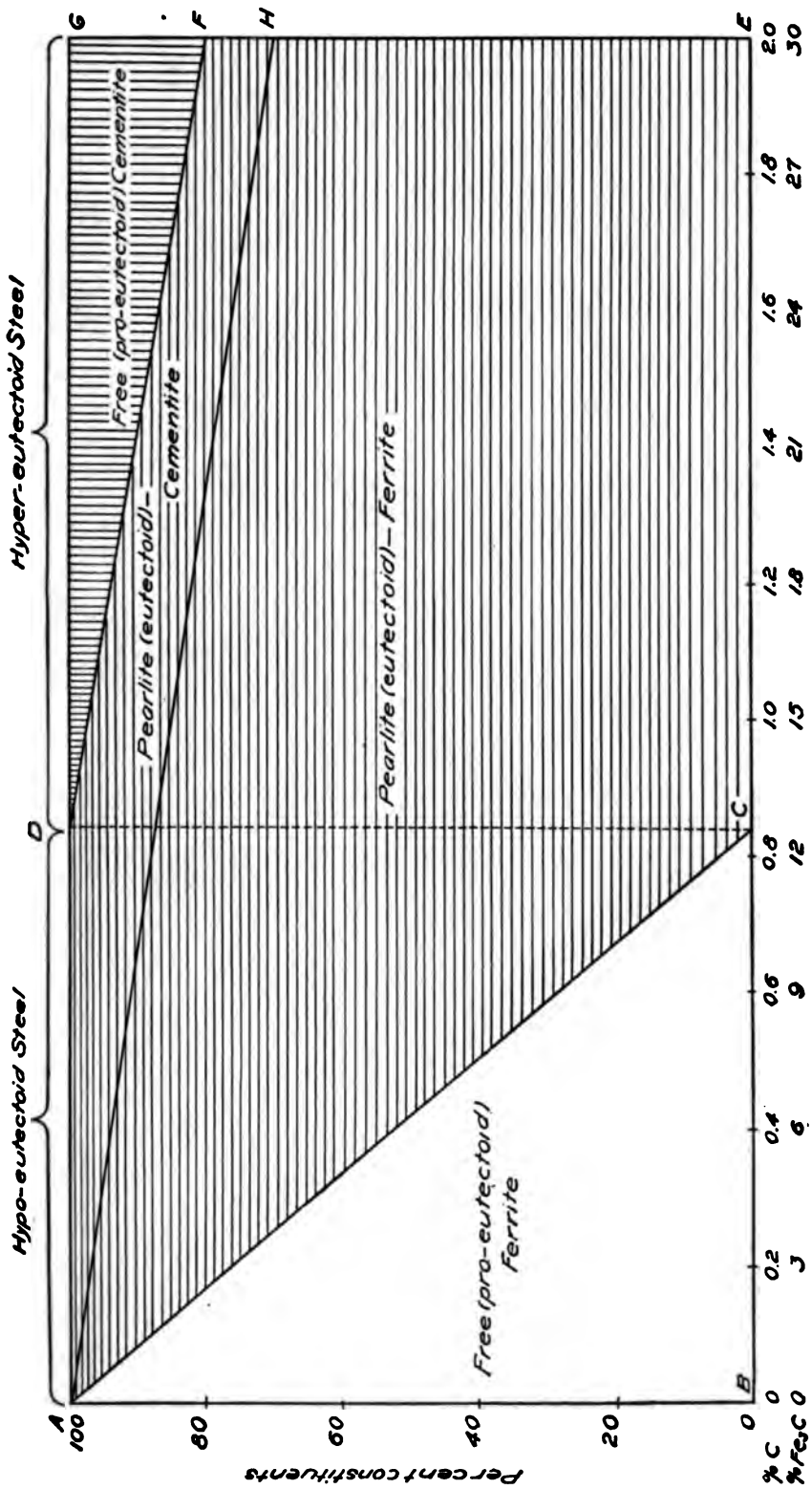


Fig. 16. — Diagram of the structural composition of slowly cooled carbon steels.

element, but it could hardly be reported as containing 0.15 or 0.35 per cent. With chemical methods on the contrary, even with the combustion method, such errors are possible, and occasionally occur, through mechanical loss, faulty manipulations, impure reagents, mistakes in weighing or figuring, etc. Chemical analysis calls for the complete destruction of the anatomy of the metal, destroying at the same time evidences of serious error; micrographic analysis, on the contrary, is based upon the anatomy itself and therefore very serious errors are quite impossible.

In order to yield results at all satisfactory, however, care should be taken that all samples be first annealed, that is reheated to 900 or 1000 deg. C. and cooled slowly, so that the normal amounts of pearlite may be formed. To attempt to apply the micro-test to forged samples for instance is certain to lead to failure. Nor can the test be applied to hypo-eutectoid steel containing but a slight amount of free ferrite, for instance to steel with from 0.60 to 0.80 per cent carbon, because of the difficulty of estimating accurately the area occupied by so small a proportion of the constituent in excess, and therefore by the pearlite itself. In the case of hyper-eutectoid steel, the differences between the contents of free cementite in steels of materially different carbon contents is so small as to resist accurate determination. For instance, steels respectively with 1.10 and 1.40 per cent carbon will contain 95.3 and 90.2 per cent pearlite, a difference of less than 5 per cent in their contents of pearlite, a quantity too small to be estimated with satisfactory accuracy under the microscope.

To sum up, the micro-test for the determination of carbon in steel, *if it is to replace chemical determinations*, should be applied only to steels containing less than some 0.60 per cent carbon which have been annealed as above stated.

The author has found the following method to yield in some instances satisfactory results: the sample after annealing and quick polishing and etching (a few small polishing scratches will not matter) is placed under the microscope, using a 16 mm. objective and a 5X eyepiece, and its image thrown on the screen of the camera. In place of the ordinary camera screen, however, another screen is substituted of ground glass, ruled into 81 squares (9 × 9), so that every square covered by pearlite evidently means very nearly 0.01 per cent of carbon in the steel (exactly 0.01 per cent carbon if we assume pearlite to contain 0.81 per cent carbon). It is then sufficient to estimate the number of squares occupied by pearlite to arrive at the carbon content of the steel. The results may be checked by estimating the carbon in two or more different spots and reporting the average if the agreement is sufficiently close.

Physical Properties of the Constituents of Steel. — It will now be timely and profitable to inquire into the physical properties of the three constituents, ferrite, cementite, and pearlite of which steel in its normal condition is composed.

It will be evident that the physical properties of commercial ferrite must resemble closely those of wrought iron and of very low carbon steel. Ferrite, therefore, is very soft, very ductile and relatively weak, having a ductility corresponding to an elongation of at least 40 per cent and a tensile strength of some 50,000 pounds per square inch. It is magnetic, has a high electric conductivity, and is deprived of hardening power, industrially speaking at least, since carbonless iron cannot be materially hardened by rapid cooling from a high temperature.

The properties of pearlite are evidently those of eutectoid steel in its normal, i.e. annealed condition, from which we may infer that pearlite has a tenacity of some [illegible] per square inch, an elongation of some 10 per cent, that it is hard, [illegible] to be explained, that it possesses maximum hardening power.

With the exception of its very great hardness little is positively known as to the physical properties of cementite. It may be assumed, however, that so hard and brittle a substance must greatly lack tenacity. Its tensile strength probably does not exceed 5000 pounds per square inch and may be considerably less, while its ductility must be practically nil. It possesses no hardening power.

These properties of the constituents of steel in its normal condition are tabulated below:

Constituents	Tensile Strength lbs. per sq. in.	Elongation % in 2 in.	Hardness	Hardening Power
Ferrite	50,000 ±	40 ±	Soft	None
Pearlite	125,000 ±	10 ±	Hard	Maximum
Cementite	5000 (?)	0	Very hard	None

Tenacity of Steel vs. its Structural Composition. — Knowing the physical properties of the three constituents of steel, it should be possible to foretell with some degree of accuracy the physical properties of any steel of known structural composition, on the reasonable assumption that these constituents impart to the steel their own physical properties in a degree proportional to the amounts in which they are present. The properties of steel made up for instance of 50 per cent ferrite and 50 per cent pearlite should be the means of the properties of ferrite and of pearlite. Let us assume such reasoning to be correct and let us apply it to the tensile strength first of hypo-eutectoid steel and then of hyper-eutectoid steel.

The tensile strength (T) of any hypo-eutectoid steel will be expressed by the following formula in function of its structural composition, that is in function of the percentages of ferrite (F) and pearlite (P) which it contains:

$$T = \frac{50{,}000\ F + 125{,}000\ P}{100}$$

in which 50,000 represents the tensile strength of ferrite and 125,000 the strength of pearlite.

Or simplifying:

$$T = 500\ F + 1250\ P$$

or again in terms of pearlite alone, since $F = 100 - P$

$$T = 500\ (100 - P) + 1250\ P$$
$$\text{or } T = 50{,}000 + 750\ P$$

or finally in terms of carbon since $P = 120\ C$

$$T = 50{,}000 + 90{,}000\ C.$$

On applying this simple formula to steels containing respectively 0.10, 0.25, and 0.50 per cent carbon we find for these metals tensile strengths respectively of 59,000, 72,500, and 95,000 pounds per square inch. These values agree closely with our knowledge of the average tenacity of such steels when in a pearlitic condition, and

formula derived from the considerations outlined above as to
between the physical properties of steel and its structural com-
borne in mind that in working out this formula it has been
contains 0.834 per cent carbon.

for various hypo-eutectoid steel should be accurate only for
termed in these lessons its normal condition, that is steel
heated to a high temperature, and slowly cooled. It should
later explained, that steel forged and finished at a fairly high
in this so-called normal condition, so that the formula
results expected, to calculate the tensile strength of such hot
be forged until its temperature is quite low and, especially,
well known that its tensile strength is generally increased.
be used, of course, in the case of hardened steel or of steel
however, be applied to steel castings which have been properly
strength may be brought up to the level of steel forgings
explained in another lesson.
is of value only in case of commercial steels containing the
impurities especially of manganese. It applies only to steels in
manganese varies roughly with the carbon content from
per cent. The presence of a larger proportion of manganese would
materially.
strength of hyper-eutectoid steel, our ignorance as to the
does not permit the writing of a formula with the same degree
assume, tentatively, however, that cementite has a tensile
pounds per square inch and then proceed as we did in the case of

strength of any hyper-eutectoid steel may be expressed by the follow-
in terms of the percentages of pearlite (P) and cementite (Cm) which it

$$T = \frac{125{,}000\ P + 5000\ Cm}{100}$$

$$T = 1250\ P + 50\ Cm$$

pearlite only, since $Cm = 100 - P$,

$$T = 1250\ P + 100\ (50 - P)$$
$$T = 5000 + 1150\ P$$

previously shown, $P = \frac{800 - 120\ C}{7}$

$$T = 5000 + 1150\ \frac{800 - 120\ C}{7}$$

$$T = \frac{955{,}000 - 138{,}000\ C}{7}$$

approximately $T = 136{,}000 - 20{,}000\ C$.

this formula to steels containing respectively 1.25 and 1.50 per cent
we find for their respective strength 111,000 and 106,000 per square inch,

which are fair values for the average tenacity of pearlitic steels of those degrees of carburization.[1]

Steel of Maximum Strength. — From the preceding considerations it seems evident that eutectoid steel must possess maximum tensile strength since the influence of the presence of ever so small an amount of free ferrite in hypo-eutectoid steel or of free cementite in hyper-eutectoid steel must necessarily be a weakening one, because of the relative weakness of free ferrite and free cementite as compared to the strength of pearlite. By most writers, on the other hand, steel of maximum tenacity is often stated to contain in the vicinity of 1 per cent carbon, that is to be slightly hyper-eutectoid.

It is not clear, however, that the results upon which the statement is based were obtained in testing steel in its *pearlitic condition.* On the contrary it seems probable that a large number of the steels tested were in a sorbitic rather than in a pearlitic condition because of relatively quick cooling through the critical range as explained in a subsequent lesson. And while it appears that pearlitic steel must have its maximum tenacity when composed entirely of pearlite, it may well be that when in a sorbitic condition maximum strength corresponds to a higher degree of carburization, i.e. 1 per cent, because sorbite may contain and indeed often does contain more carbon than pearlite. Indeed the cases on record show that when the steels were made pearlitic through very slow cooling maxium tenacity corresponds closely to the eutectoid composition. Arnold, for instance, tested a series of very pure carbon steel and after slow cooling in the furnace from 1000 deg. C he found a very sharp maximum in the tenacity corresponding to 0.89 per cent carbon. On cooling these same steels in air, on the contrary, and therefore making them sorbitic, maximum tenacity corresponded to 1.20 per cent carbon. Harbord likewise ascertained the tenacity of very pure steels and found after slow cooling (in the furnace) from 900 deg. C that the maximum tenacity corresponded to 0.947 per cent carbon.

Ductility of Steel vs. Its Structural Composition. — From the known ductility, as expressed by its elongation under tension, of ferrite and the known elongation of

[1] Empirical formulas have often been suggested to express the relation between the tenacity of steel and its carbon content. Deshayes proposed for unannealed steel

$$T = 30.09 + 18.05\ C + 36.11\ C^2$$

Thurston (minimum values) for unannealed steel

$$T = 42.32 + 49.37$$

and for annealed steel

$$T = 35.27 + 42.32$$

Bauschinger for Bessemer steel

$$T = 43.64\ (1 + C^2)$$

Weyrauch (minimum values)

$$T = 44.17\ (1 + C)$$

Salom (average values)

$$T = 31.74 + 70.53\ C.$$

The above formulas express the tenacity in kilograms per square millimeter. Campbell, for acid open hearth steel, gives

$$T = 40.000 + 1000\ C + 1000\ P + xMn + R$$

and for basic open hearth steel

$$T = 41.500 + 770\ C + 1000\ P + yMn + R$$

in which x and y are values given in a table and dependent upon the percentage of manganese and of carbon present. R is a variable to allow heat treatment.

... respectively 40 and 10 per cent in two inches, it should be possible to work ... expressing the ductility of any hypo-eutectoid steel in the annealed ... condition. In terms of ferrite and pearlite the ductility should be

$$D = \frac{40\,F + 10\,P}{100}$$

$$D = .4\,F + .1\,P$$

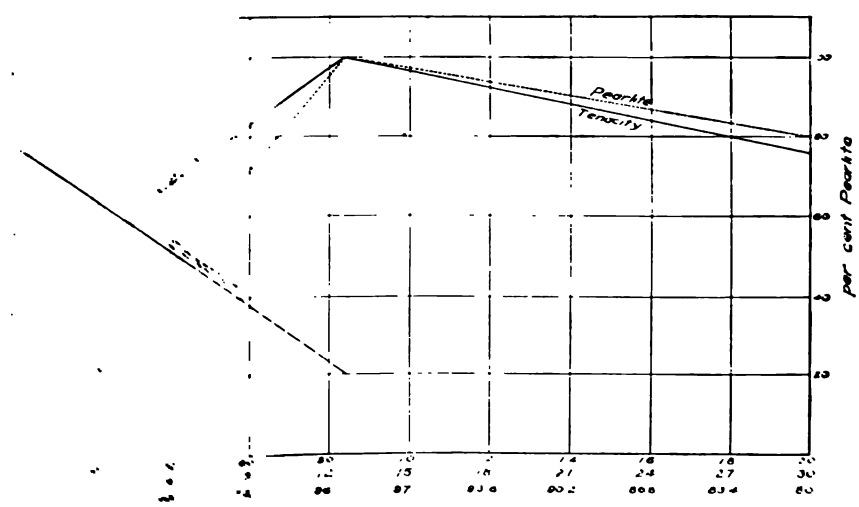
... ductile alone since $F = 100 - P$

$$D = .4\,(100 - P) + .1\,P = 40 - .3\,P$$

... the ductility in terms of carbon will be

$$D = 40 - 36\,C$$

... instance, containing 0.25 and 0.50 per cent carbon should have ... of 31 and 22 per cent.[1]



... showing the relation between the tenacity and ductility of annealed (pearlitic) steels and the carbon content.

... compare this formula with some others that have been proposed. Howe ... inches of steel under 0.50 per cent carbon

$$D = 33 - 60\,(C^2 + 0.1)$$

... and 1.00 per cent carbon:

$$D = 12 - 11.9\sqrt[3]{C} - 0.5$$

... inches, gives

$$D = 42 - 56\,C$$

... inches

$$D = 35 - 30\,C$$

... values for the elongation of steel than the author's formula, but all indi- ... that they refer to steel in a rather sorbitic condition and, therefore, more ... whereas the formula here suggested is for truly pearlitic steel only.

Diagram Showing the Relation Between the Tenacity and Ductility of Steel and Its Carbon Content. — By plotting the formulas suggested in this lesson to express the relation between the carbon content of steel and its tenacity and ductility the curves of Figure 17 are obtained. To the tenacity and ductility curves a third curve has been added showing the variation of the amount of pearlite with the carbon content.

Experiments

The student should procure five samples of forged steel of good commercial quality, containing respectively about 0.30, 0.50, 0.85, 1.25, and 1.50 per cent carbon. These should be heated to 900 or 1000 deg. C. and slowly cooled from that temperature. Specimens should be cut from the treated samples and prepared for microscopical examination in the usual way.

Etching. — Any one of the three methods described in Lessons III and IV may be applied with satisfactory results. The student is advised to use the method which, in connection with the experiments of the two previous lessons, he has found to give the best results.

Examinations. — All samples should be carefully examined, firstly with low power objectives and secondly with high power objectives. Observation under low power should in all cases reveal clearly and sharply the pearlite and ferrite areas in hypo-eutectoid steel, the pearlite and cementite areas in hyper-eutectoid steel. Examination under high power, 300 diameters or more, should satisfactorily reveal the structure of the pearlite. In the case of the eutectoid steel, low power observation will reveal but an indistinct structure, because of the absence of any free ferrite or cementite and of the fineness of the pearlite structure.

Etching with Sodium Picrate. — The hyper-eutectoid steels should be rubbed on the rouge block or disk so as to efface the pattern produced by the etching and treated with a boiling solution of sodium picrate in an excess of sodium hydroxide in order to color darkly the free cementite. The instructions given in the lesson for this operation should be followed.

Photomicrography. — All samples should be photographed both with low and high power objectives. In taking low power photomicrographs the directions given in Lesson IV should be followed.

For the taking of high power photographs a 4 mm. (1/6 in.) objective and a 5X (2 in.) or if needed a 10X (1 in.) eyepiece are recommended. With the camera screen some 15 inches from the eyepiece a magnification of 325 diameters will be obtained in case of the 5X eyepiece and of 650 diameters with the 10X eyepiece.

The needed manipulations for the taking of high power photomicrographs are the same as to their nature as those required for taking low power photographs but they call for much greater accuracy. The adjustment of the source of light and of all parts used in condensing the light, including the vertical illuminator should be done with the greatest possible care and delicacy while the focusing of the image on the camera screen could hardly receive too much attention. The student is urged not to be discouraged if his first attempts at taking high power photomicrographs are failures. Patience, perseverance, and experience will eventually lead to the mastery of the manipulations required for successful high power photomicrography of metal sections.

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...ectoid, and of hyper-eutectoid

...on, what will be the proximate
...spectively 0.12, 0.27, 0.56, and
...imate structural composition?

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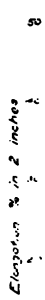

LESSON VI

IMPURITIES IN STEEL

Metallic Impurities. — Commercial grades of steel always contain, besides carbon, varying amounts of silicon, phosphorus, sulphur, and manganese, often an appreciable proportion of copper and traces at least of many other metals and metalloids. These may be called the metallic impurities.

Non-metallic or Oxidized Impurities. — Non-metallic or oxidized impurities, chiefly oxides and silicates of iron and manganese, are also frequently found in steel, principally through the retention by the metal of some of the slag produced during the refining operation. Hibbard has recently suggested the name of "sonims" for this class of impurities.

Metallic vs. Non-metallic Impurities. — There is a sharp distinction between the behavior of metallic and non-metallic impurities, the former forming true alloys with the contaminated metal, the latter being merely inclusions, their union with the metal being purely mechanical.

Gaseous Impurities. — Steel always contains some gases, apparently held in solution and called "occluded" gases, chiefly hydrogen, nitrogen, and carbon monoxide (CO).

Impurities vs. Physical Properties of Steel. — It is well known that surprisingly small proportions of some of the metallic impurities just mentioned have a very marked influence upon the physical properties of steel. Some 0.2 per cent phosphorus, for instance, renders many grades of steel so brittle as to unfit them for most commercial uses. And as it is logical to suppose that there exists a very close relation between the structure of a metal and its physical characteristics, we naturally expect to find important structural changes corresponding to marked alterations of physical properties. We should expect, for instance, the structure of a high phosphorus, brittle steel to be quite different from the structure of a low phosphorus, tough steel of otherwise identical composition. In the present state of metallography the microscope does not always reveal such differences of structures as we are led to look for. We may reasonably anticipate, however, that, as the science progresses, structural differences will be detected of a magnitude fairly in keeping with the deep changes of physical properties brought about by slight changes of chemical composition. Indeed in recent years material advance has been made in this direction and the influence of the usual impurities upon the properties of steel has been on the whole satisfactorily accounted for by metallographic methods as will be apparent from the description which follows.

Silicon in Steel. — All grades of steel contain a trace at least of silicon (Si) and occasionally as much as 0.5 per cent, and even more, most grades containing between 0.05 and 0.3 per cent.

When present in such small proportion silicon is entirely dissolved in the iron with which it forms a solid solution. It is probable, however, that it is not held in solution by the iron in its elementary condition, Si, but rather as a silicide of iron, FeSi. Since the atomic weight of iron is 56 and that of silicon 28 it will be evident that 28 parts by weight or silicon produces 56 + 28 or 84 parts by weight of FeSi, or that silicon produces exactly 3 times its own weight of FeSi $\left(\frac{84}{28} = 3\right)$. For instance 0.1 per cent silicon in the steel will give rise to the formation of 0.3 per cent of FeSi and this small amount of iron silicide will be held in solid solution by the iron. The ferrite of commercial steel, therefore, always contains a small amount of silicon in the form of an iron silicide, and let it be borne in mind that this applies to the ferrite forming part of the pearlite of all slowly cooled steels as well as to the free ferrite of hypo-eutectoid steel.

It has been stated in another lesson that when an impurity forms a solid solution with the contaminated metal, changes of crystalline forms are not generally observed. This is true in the present case for there is apparently no structural difference between a steel with some 0.3 or 0.4 per cent silicon and a steel nearly free from that element but otherwise of identical composition. The presence of silicon in steel cannot as yet be satisfactorily detected, even qualitatively, by metallographic methods, although we have the unquestionably accurate statement of Le Chatelier that silicon causes ferrite to etch more slowly.

In view of the similarity of structure between steel containing much silicon (i.e. several tenths of 1 per cent) and steel practically free from it, we should expect that the presence of a small amount of silicon cannot affect materially the properties of steel, and this we know to be the case.

Phosphorus in Steel. — Steel of satisfactory quality contains from a trace to 0.1 per cent of phosphorus (P). As in the case of silicon this small amount of phosphorus is held in solid solution by the iron, not, however, in the elementary state, P, but as the phosphide of iron Fe_3P. The atomic weight of iron being 56, that of phosphorus 31, and the phosphide containing three atoms of iron for each atom of phosphorus, it will be obvious that 31 parts by weight of phosphorus will form $3 \times 56 + 31$ or 199 parts of the phosphide Fe_3P, or roughly, 1 part by weight of phosphorus will give rise to the formation of 6 parts of phosphide. For instance, the presence in steel of 0.05 per cent phosphorus results in the formation of 0.3 per cent of Fe_3P held in solid solution by the ferrite, this being true of the ferrite included in the pearlite of all slowly cooled steel as well as of the free ferrite of hypo-eutectoid steel.

While phosphorus in common with other metallic impurities forming solid solutions does not alter the crystalline form of steel, it is generally believed to have a marked tendency to enlarge the grains of the metal, which tendency would account for the well-known brittleness imparted to steel by phosphorus when present in excess of 0.1 per cent. The brittleness caused by a large grain will be considered further in another lesson.

Except for this enlargement of the grains, microscopical examination does not reveal the presence of the usually small percentages of phosphorus occurring in steel, although it is said by some writers that phosphorus as well as manganese causes ferrite to etch darker.

Sulphur in Steel. — Steel of satisfactory commercial quality may contain from a mere trace to some 0.1 per cent sulphur, generally between 0.01 and 0.05 per cent —

It is universally known that manganese and sulphur have very great reciprocal affinity so that when brought together at a high temperature they combine chemically with each other to form the sulphide of manganese, MnS. This is what happens in steel which always contains manganese as well as sulphur. From the atomic weight of manganese, 55, and that of sulphur, 32, it will be seen that 32 parts by weight of sulphur produces 87 parts of MnS, or approximately 2½ parts of sulphide for each part of sulphur. Steel with 0.05 per cent sulphur, for instance, will contain about 0.125 per cent of MnS, provided, of course, there is enough manganese present to satisfy the sulphur which must necessarily be so in properly made steel.

The existence of the sulphide of manganese, MnS, in steel has been conclusively proven. In steel castings it occurs as rounded areas the color of which is generally described as pale or dove gray or slate color. In forgings it occurs in elongated particles, bands, or strings of the same tint, running parallel to the direction of the forging or rolling (Figs. 1 and 2).

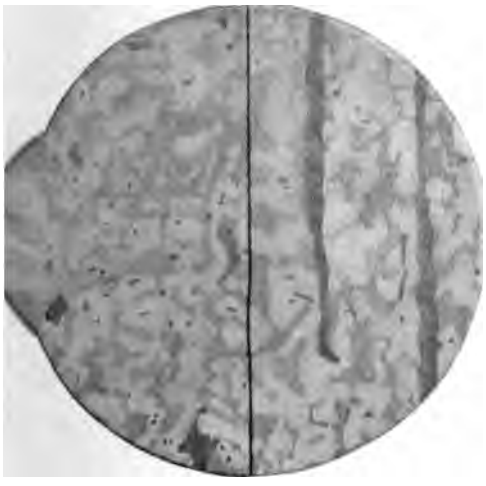

Fig. 1.—Steel. Carbon 0.46 per cent. Manganese 1.07 per cent. Sulphur 0.54 per cent. Forged, reheated to 1200 deg. C. and cooled in air. Magnified 460 diameters. Right half section is longitudinal (direction of rolling), the left half is transverse. (Arnold.)

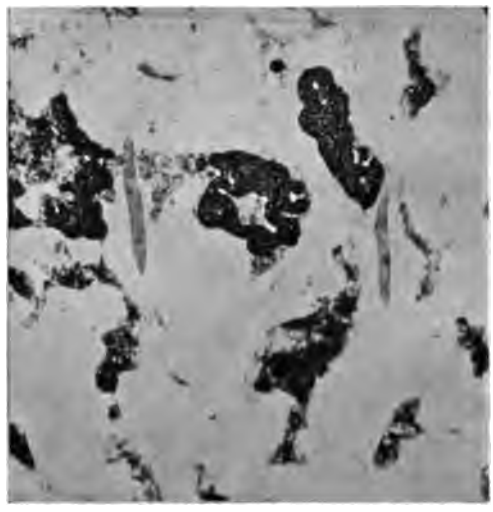

Fig. 2. — Steel. Hypo-eutectoid. Manganese sulphide in ferrite areas. Magnified 300 diameters. (Levy.)

According to Le Chatelier MnS has a melting-point superior even to that of iron, solidifying, therefore, first, and the bulk of it rising to the top of the bath or ingot, the manganese is in this way helpful in removing sulphur from steel. Some writers, however, question this higher melting-point of MnS. Levy reports that the melting-point of pure MnS is probably not far from 1400 deg. C., and, therefore, below the melting-point of hypo-eutectoid steel at least, while the presence of some FeS would lower materially its melting-point. It appears probable that the solidification of the sulphide must follow and not precede that of the iron.

This view seems to be supported by the location of the sulphide particles at the boundaries of the pearlite grains of eutectoid steel, in the free ferrite of hypo-eutectoid steel or in the free cementite of hyper-eutectoid steel. What MnS is retained by the solid steel, since it occurs as shown in the shape of small individual grains or

elongated particles, can only injure the metal through breaking up its continuit and, in view of the very small amount of sulphur, and, therefore, of MnS, present i steel of good quality, it is evident that this breaking up and its action upon the pro erties must be very slight. This is in agreement with the known fact that a sma amount of sulphur in steel containing also the proper amount of manganese has n appreciably injurious effect.

Seeing that steel seldom contains much more than some 0.05 per cent sulphu hence more than 0.125 per cent MnS, it is not to be expected that this compoun will generally be detected in polished and etched steel sections. Indeed whenev detected it points to a segregation of the sulphide together with other impuriti (ghost lines) as described later.

In case sulphur occurs in excess over the amount needed to form the sulphic MnS with the manganese present in the steel, the excess sulphur, that is the sulph left over after satisfying the manganese, combines with some of the iron, forming th iron sulphide FeS. It should be noted at once, however, that it requires less tha 2 parts by weight of manganese (atomic weight 55) to combine with 1 part of sulph (atomic weight 32). In other words if the steel contains twice as much manganes as it does sulphur, this should theoretically be enough to convert the whole of th sulphur into the sulphide MnS. As it is very seldom indeed that steel does not co tain a much larger proportion of manganese than that compared to its sulphur co tent, the occurrence of free FeS in steel should be very rare. It is not to be expecte in metal of good quality, its presence pointing to a very abnormal compositio namely high sulphur content and very low percentage of manganese. According t Levy, however, MnS and FeS are readily soluble in each other in the solid state, Mn being capable of holding as much as 50 per cent of FeS in solid solution. Accordin to this writer MnS is seldom free from FeS even when the steel contains considerab manganese, the mass action exerted by the presence of so large a proportion of iro preventing the manganese from taking hold of the totality of the sulphur in spite its greater affinity for it. MnS nearly free from FeS appears quite dark, while i color becomes lighter and more yellowish as the proportion of FeS increases. Lev notes also that in high carbon steel the MnS areas are generally colored darker tha in low carbon steel, indicating greater freedom from FeS, apparently owing to th fact that in high carbon steel the mass action exerted by iron is not so great since contains less iron.

The sulphide FeS exhibits a marked tendency to form continuous envelopes membranes surrounding each grain of pearlite (Fig. 3), and probably consisting of eutectic alloy of iron and iron sulphide (the composition of the eutectic is apparentl FeS 85 per cent, Fe 15 per cent). These membranes being weak and brittle impa weakness and brittleness to the steel. The well-known red-shortness caused by su phur in the absence of a sufficient amount of manganese (to form MnS) is probabl due to the low melting-point (950 deg. C. according to some writers) of this iro iron sulphide eutectic. At a high temperature the melting of this eutectic destro the cohesion between the grains of the metal resulting in cracks being developed du ing the process of forging or rolling, and in extreme cases in the metal actually breal ing into several pieces. The presence of a large amount of FeS in some Bessemer ste at the end of the blow, before the addition of manganese, is undoubtedly largely r sponsible for the marked red-shortness of the metal at this stage of the operation.

Under the microscope FeS appears yellow or pale brown. Tests showing th

presence of sulphur in the constituents described above as sulphides may be conducted as follows, provided they occur in sufficiently large particles: A sheet of silver bromide (photographic) paper should be pressed upon the polished section and moistened with sulphuric acid when the sulphur present will be evolved as H_2S (sulphuretted hydrogen) and will darken the paper. Another method (Law) consists in covering the section with a coating of gelatine containing an acid solution of lead or cadmium salt; the acid decomposes the sulphide forming H_2S which produces a deep brown or yellow stain of lead or cadmium sulphide, PbS or CdS.

Manganese in Steel. — It has been seen that manganese combines readily with sulphur and that the resulting manganese sulphide, MnS, can be detected in polished steel sections as a pale or dove gray constituent assuming the shape of rounded areas in castings and of bands or threads in forgings. Manganese silicate is also occasionally

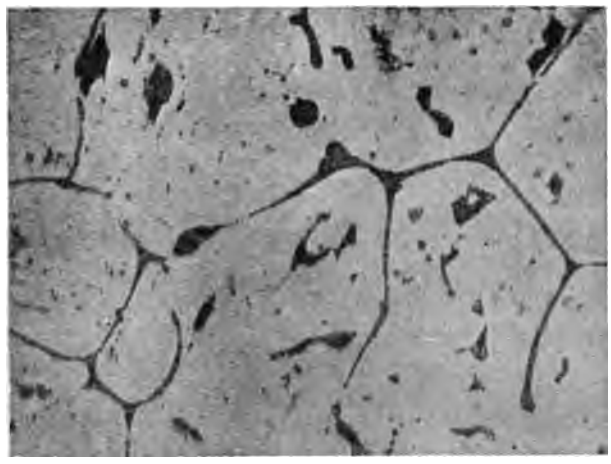

Fig. 3. — Red short steel. Magnified 300 diameters. Sulphur 0.54 per cent. Unetched. Network of FeS. (Ziegler.)

found in steel as later explained and may sometimes be mistaken for MnS. Satisfactory tests for the distinction of these two constituents will be described.

When manganese occurs in excess over the amount required to form MnS with the totality of the sulphur present, as is almost universally the case, the manganese in excess combines with some of the carbon to form the carbide of manganese, Mn_3C, and this carbide is found associated with the iron carbide, Fe_3C, in cementite. The cementite of commercial steel, therefore, is seldom a pure iron carbide, containing, on the contrary varying amounts of Mn_3C. Since iron and manganese have practically the same atomic weight, however (55 and 56 respectively), it remains practically true that carbon forms 15 times its own weight of cementite, even when the latter contains a large proportion of Mn_3C.

There is no metallographic test by which cementite free from manganese can be distinguished from cementite rich in Mn_3C.

Some authors mention the possible presence of the manganese silicide, MnSi, in steel, while solid solution between manganese and iron is frequently referred to. While manganese and iron (ferrite) undoubtedly form solid solutions, it does not seem likely that these are produced when manganese is present in small proportion,

say not over 1 per cent. In that case it seems more probable that manganese is found in the two forms described above, (1) as a manganese sulphide MnS, containing practically the totality of the sulphur in steel of good quality, that is, containing not over 0.05 per cent sulphur and not less than 0.25 per cent manganese, and (2) as the manganese carbide Mn_3C, associated with Fe_3C in cementite.

Chemical vs. Structural Composition. — Knowing the probable chemical forms of the five metallic impurities always present in steel, carbon, silicon, phosphorus, sulphur, and manganese, as well as their structural associations, it will be interesting and profitable to consider accordingly the proximate chemical composition as well as the ultimate and proximate structural compositions of a steel of known ultimate chemical composition. Let us assume a steel of the following ultimate chemical composition:

C	0.50	per cent
Mn	0.80	" "
S	0.05	" "
P	0.04	" "
Si	0.10	" "
Fe (by diff.)	98.51	" "
	100.00	

Bearing in mind the atomic weights of these elements (Fe, 56; C, 12; Mn, 55; S, 32; P, 31; Si, 28) and the formulas of the chemical compounds formed (MnS, FeSi, Fe_3P, Mn_3C, Fe_3C), it will be readily seen that:

(1) 0.05 per cent S will give rise to the formation of 0.13 per cent MnS.
(2) 0.13 per cent MnS contains about 0.08 per cent Mn.
(3) This leaves 0.80 − 0.08 = 0.72 per cent manganese in excess to combine with C.
(4) 0.72 per cent Mn will form 0.77 per cent Mn_3C.
(5) 0.77 per cent Mn_3C contains about 0.05 per cent carbon.
(6) This leaves 0.50 − 0.05 = 0.45 carbon to combine with iron.
(7) 0.45 per cent carbon results in the formation of 6.75 per cent of Fe_3C.
(8) 0.04 per cent of P corresponds to about 0.25 per cent of Fe_3P.
(9) 0.10 per cent Si gives 0.30 per cent FeSi.

The proximate chemical composition of the steel considered will be

Fe_3C	6.75	per cent
Mn_3C	0.77	" "
Fe_3P	0.25	" "
FeSi	0.30	" "
MnS	0.13	" "
Fe (by diff.)	91.80	" "
	100.00	

As to the ultimate structural composition of the steel, we know that the cementite contains the Fe_3C and the Mn_3C hence we have 6.75 + 0.77 = 7.52 per cent cementite. In pure steel the percentage of cementite would have been 0.50 × 15 = 7.50 per cent. The slight difference between the two numbers is due to the presence of manganese in the commercial steel, and to a slight difference between the atomic

weights of manganese and that of iron (55 compared to 56), a difference so slight that for all practical purposes we may assume that in commercial steels as well as in pure steel the percentage of carbon multiplied by 15 gives the amount of cementite formed. The total ferrite present in this steel contains all the free iron, as well as the small proportions of Fe_3P and FeSi present, hence this steel contains 91.80 + 0.25 + 0.30 = 92.35 total ferrite. In pure steel the proportion of total ferrite would have been 100 – 7.50 or 92.50 per cent. The difference between the two values is evidently due to the presence of a trifle greater amount of cementite, and to the presence of 0.13 per cent MnS.

The ultimate structural composition of the steel under consideration is, therefore:

Cementite	7.52
Total ferrite	92.35
MnS	0.13
	100.00

Finally its proximate structural composition will be, since the pearlite of hypo-eutectoid steel contains 8 times the weight of total cementite (assuming the eutectoid carbon point to be 0.834 per cent):

Pearlite 7.52 × 8 =	60.16
Free ferrite (by diff.)	39.71
MnS	.13
	100.00

Ignoring the presence of impurities the quick method described in Lesson V would have given pearlite 60 per cent, ferrite 40 per cent, i.e. values which may be considered identical for any practical purposes. It follows from this that in calculating the structural composition of any carbon steel of ordinary commercial quality the presence of the impurities need not be considered; the steel may be treated as if it was made exclusively of iron and carbon.

The relation between chemical and structural compositions, both ultimate and proximate, is further shown in the following table.

CHEMICAL COMPOSITION				STRUCTURAL COMPOSITION			
Ultimate		Proximate		Ultimate		Proximate	
	%		%		%		%
Fe(by diff.)	98.51	Fe(by diff.)	91.80	Total Ferrite	92.35	Free Ferrite	39.71 Free Ferrite
Si	0.10	FeSi	0.30			Pearlite Ferrite	52.64 60.16% Pearlite
P	0.04	Fe_3P	0.25				
C	0.50	Fe_3C	6.75	Cementite	7.52	. . . . .	
Mn	0.80	Mn_3C	0.77				
S	0.05	MnS	0.13	MnS	0.13	. . . . .	0.13
	100.00		100.00		100.00		100.00

Non-Metallic or Oxidized Impurities. — As already mentioned steel not i quently contains small amounts of non-metallic or oxidized impurities, chiefly and manganese oxides and silicates, derived mainly from the retention by the r

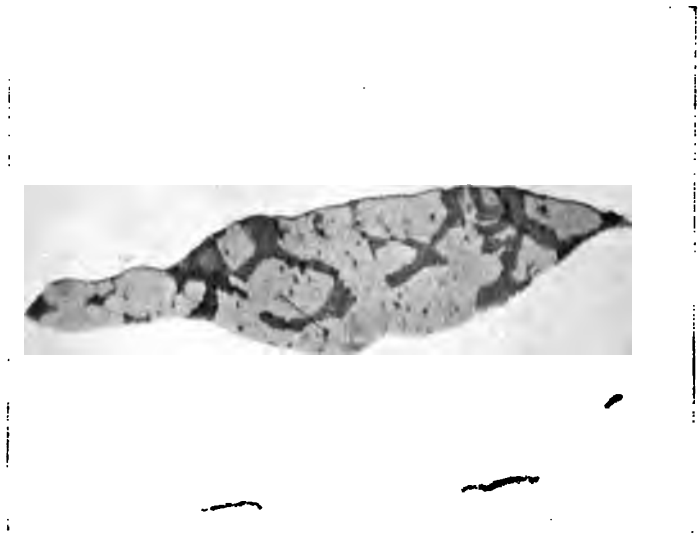

Fig. 4. — Manganese sulphide (light constituent) and manganese silicate in steel. Magnified 1000 diameters. (Law.)

Fig. 5. — Manganese sulphide (light constituent) and iron silicate in mild steel. Unetched. Magnified 1000 diameters. (Law.)

in the shape of minute particles of some of the slag formed during the proce manufacture. Their mode of occurrence is very different from that of the me impurities just examined (with the exception of MnS which behaves more like a metallic than like a metallic impurity). These oxidized impurities do not alloy

the metal; their association with it remains a purely mechanical one, like small pebbles in a mass of clay. These oxides and silicates commonly occur as rounded or slightly elongated particles and can generally be detected in the polished section before etching.

Manganese silicate, probably $2MnO.3SiO_2$, and manganese sulphide, MnS, which occasionally occur together, have a somewhat similar appearance, care being required in order to differentiate between them, although the former is as a rule decidedly darker (Fig. 4). Stead recommends the placing of a drop of sulphuric acid on the polished specimen, when H_2S gas will be evolved where MnS is present, particles of silicates of manganese, on the contrary, evolving no gas. The dissolving of MnS also leaves pits. Stead also advises heat tinting as the best means of distinguishing between the sulphide and the silicate, the heating to be continued until the specimen has assumed a light brown coloration, when the MnS remaining bright can be sharply differentiated from the silicate.

According to Levy, sulphide and silicate of manganese are readily soluble when

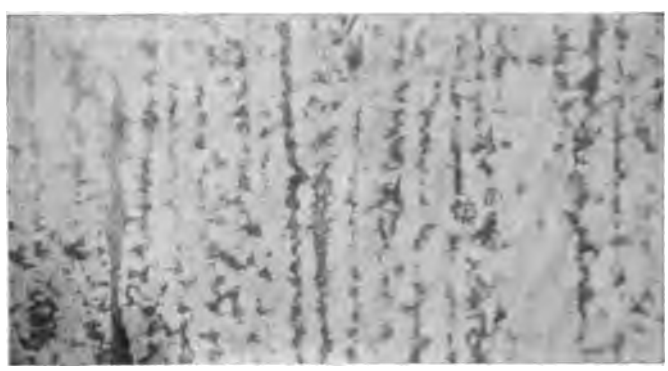

Fig. 6. — Ghost lines in low carbon steel. Magnified 95 diameters. (Boylston.)

molten but on solidifying the sulphide crystallizes in well-marked dendritic forms, the resulting mixture of sulphide and silicate (Fig. 4) resembling slag inclusions (see Lesson III, Fig. 5).

Manganese sulphide and iron silicate may also occur in close vicinity, the latter constituent being darker and frequently broken in many irregular fragments by the working of the metal (see Fig. 5).

At the end of the refining operation by which steel is produced, especially towards the latter part of the Bessemer blow, a considerable amount of iron oxide is formed and in spite of the steps taken for removing it from the bath (addition of manganese, etc.) some of it, occasionally quite a little, is retained by the metal, when it is a source of red-shortness besides having other detrimental effects. This iron oxide generally occurs as small dark points readily detected in the polished section before etching.

For further treatment of polished sections with a view of identifying oxidized impurities, the student is referred to Lesson III where the constitution of slag in iron has been treated at some length.

Gaseous Impurities. — It has not been possible so far to detect the presence of occluded gases in steel by means of metallographic methods. While the problem

seems a very difficult one to solve, the statement that it can never be solved wo not be justified for the discovery of some metallographic treatment by which a me rich in certain gases may be distinguished from a similar metal free from them is w within the limits of reasonable expectation.

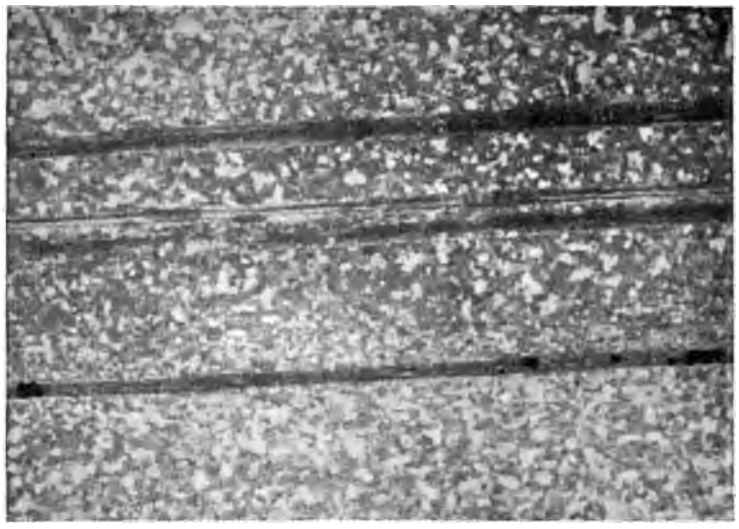

Fig. 7. — Ghost lines in low carbon steel. Magnified 10 diameters. (Law.)

Fig. 8. — Ghost lines in low carbon steel. Magnified 200 diameters. (Law.)

Segregation of Impurities. — Ghosts. — The very small proportions of impurit generally found in steel of good quality have little, if any, injurious effect upon most important and useful physical properties, so long as they remain uniform distributed throughout the metallic mass, i.e. so long as the steel is chemically hon geneous. These impurities, on the contrary, may become extremely injurious wl

they show a tendency to "segregate," i.e. to collect in certain portion or portions of steel castings and forgings, when the segregated portions may contain so large an amount of impurities as to have their useful properties utterly destroyed. Segregated metal is generally brittle, weak, and hard.

Under the microscope a metal suffering from this segregation of impurities generally is found to contain bands of varying widths and lengths, technically known as "ghosts" or "ghost lines," in which the presence of abnormally large proportions of MnS, phosphorus, and carbon can generally be detected by the ordinary metallographic tests, these (S, P, and C) being the three impurities showing the greatest tendency to segregate. Photomicrographs of ghost lines are shown in Figures 6, 7, 8, and 9. Ghost lines etch more rapidly than the surrounding metal therefore appearing darker

Fig. 9. — Ghost lines in low carbon steel. Magnified 2000 diameters. Manganese sulphid and pearlite particles. (Law.)

after etching even to the naked eye. These lines can generally be detected before etching because of the manganese sulphide which they contain.

Bannister mentions two kinds of ghost lines, (1) those showing marked segregation of C, S, and P, and considerable Si and Mn and (2) those containing little Si and Mn. Houghton, on the other hand, refers to ghost lines containing S and P but no carbon.

Experiments

High vs. Low Phosphorus Steel. - The student should procure two samples of forged steel containing preferably from 0.30 to 0.50 per cent carbon and of nearly identical composition, except as to phosphorus content which should be high in one sample (if possible considerably more than 0.1 per cent), and low in the other (not over 0.05 per cent). These samples should be heat treated in the usual way so that they may assume their normal structure and a specimen prepared from each sample for microscopical examination etching them with picric or nitric acid in alcohol or with concentrated nitric acid according to individual preference. Upon being ex-

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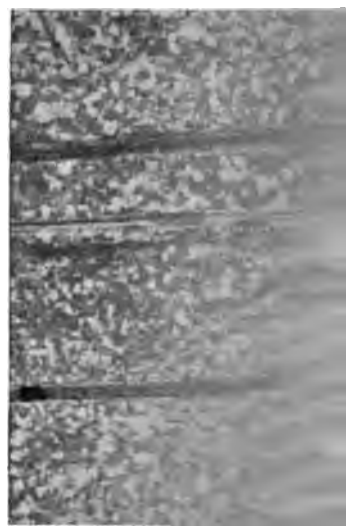
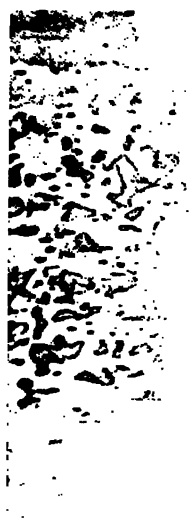


Fig. 7. — Ghost lin[illegible]



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LESSON VII

THE THERMAL CRITICAL POINTS OF STEEL

THEIR OCCURRENCE

The structure of steel described in the preceding lessons, i.e. its normal structure, is greatly affected by the treatment or treatments, both mechanical and thermal, to which the metal may be subjected during the process of manufacture of finished objects. It is to the close relation existing between the treatment and the structure on the one hand, and between the structure and the physical properties of the metal on the other, that metallography owes its industrial importance. It is essential, therefore, that the student should have a clear understanding of these relations. As a preparation to this important study, however, it will be necessary to describe a phenomenon of the greatest moment in the treatment of steel, namely, the occurrence of spontaneous absorptions or evolutions of heat during the heating or cooling of the metal. These are generally termed the "thermal" critical points or simply "critical points," also "retardations," "transformation" points, and "critical temperatures."

Point of Recalescence. — If a piece of steel containing some 0.60 per cent carbon be heated to a high temperature, say to 1000 deg. C., and allowed to cool slowly from that temperature, and if its rate of cooling be carefully ascertained, conveniently by means of a Le Chatelier pyrometer, it is found that the cooling proceeds at first at a nearly uniformly retarded rate. If, for instance, it requires 10 seconds for the metal to cool through the first five degrees (from 1000 to 995 deg.), and 12 seconds to cool through the next five degrees (995 to 990 deg.), it will require some 14 seconds for the next five degrees, 16 seconds for the following five, and so on, the cooling through each range of five degrees being a little slower than the preceding cooling of five degrees. All cooling bodies, whatever their nature, generally follow this law. The plotting of time and temperature as coordinates yields smooth curves, sometimes approaching straight lines (see curve B, Fig. 9).

In the case of the steel we are now considering, when a certain temperature is reached, in the majority of cases some 650 to 700 deg. C., a most interesting and significant phenomenon takes place; the cooling of the metal is momentarily arrested, the pyrometer, for a certain length of time, failing to record any further fall of temperature. Indeed, when the circumstances are favorable, the temperature of the cooling mass actually rises; the metal becomes visibly hotter; it "recalesces," hence the name of "recalescence" given to this thermal critical point. If the experiment be conducted in a dark room, this recalescence or spontaneous glow of the steel is plainly visible. After a while the metal resumes its normal rate of cooling which is then continued down to atmospheric temperature.

It is evident that at this critical point the surrounding atmosphere does not cease to abstract heat from the piece of steel, and, since its temperature nevertheless

remains stationary or even rises, it must be that heat is here spontaneously generated within the metal in amount sufficient to make up, or more than make up, for the heat lost by radiation and conductivity.

In heating, as might be expected, the reverse phenomenon takes place: an *absorption* of heat causing a retardation in the *rise* of the temperature, or even a momentary stop, the pyrometer failing for a few moments to record any further increase of temperature or recording only an abnormally low increase, although heat continues to be applied to the steel at the same speed. Actual *lowering* of the temperature of the steel is not generally observed at this critical point on heating, i.e. the steel does not grow perceptibly colder.

Notation. — Osmond, who was the first to determine accurately the position and magnitude of the point of recalescence and who is the discoverer of the upper critical points soon to be described, adopted Tschernoff's previous notations, and designated the critical points by the letter A.[1] To distinguish critical points on cooling from those occurring on heating the former are called Ar (from the French *refroidissement*, meaning cooling) and the latter Ac (from the French *chauffage*, heating). To distinguish further between the point of recalescence and its reversal on heating on the one hand, and critical points occurring at higher temperatures on the other, the notations Ar_1 and Ac_1 are used for the recalescence point and its reversal, and Ar_2, Ac_2, Ar_3, Ac_3 for the two upper reversible critical points soon to be described. The notations A_1, A_2, A_3 are frequently used when the points and their reversals are considered collectively. By the notation A_1, for instance, is meant the point of recalescence Ar_1 and its reversal Ac_1. These notations will be used in these lessons.

Brinell, in his important work on the heat treatment of steel, used the letter V for the point of recalescence and W for its reversal on heating. These symbols, however, are now very seldom used.

The expression "point of recalescence" is frequently used indifferently for the point on cooling, where heat is evolved causing a recalescence of the metal, and for the reverse phenomenon on heating, at Ac_1, where, of course instead of a recalescence taking place, an absorption of heat occurs causing the metal to *lose* heat. It is obvious that the term recalescence should not be applied to the point Ac_1. The point of recalescence is also called sometimes recalescent point and, seldom, Gore's phenomenon (see Historical Sketch at end of lesson). The point Ac_1 has been called point of "decalescence" by some writers and one of them at least refers to it as the "calescence" point.

Critical Range. — Transformation Range. — When the various critical points occurring in steel are considered collectively the range of temperature they cover is frequently called the critical range, or, more seldom, but very appropriately, the transformation range. It will soon be shown that the critical range may include one two, or three critical points. The meaning of the expressions "critical range on heating" and "critical range on cooling" is obvious.

Positions of Ar_1 and Ac_1. — The critical points Ar_1 and Ac_1 do not occur at exactly the same temperature, Ac_1 being generally situated some 25 to 50 deg. higher than Ar_1. When the point Ar_1, for instance, is found at 690 deg. C., the point Ac_1 will generally occur somewhere between 715 and 740 deg. It does not follow, however, that these two points are not the opposite phases of the same phenomenon

[1] The point A of Tschernoff indicated the temperature at which steel suddenly acquires hardening properties on heating or loses them on cooling.

The fact that the critical point on cooling lags behind the point on heating and vice versa, is evidently a case of hysteresis so often observed in physical phenomena and which implies a resistance of certain bodies to undergo a certain transformation, when theoretically the transformation is due, the delayed transformation finally taking place with added violence. This was vividly depicted by Howe some twenty years ago in the case of iron. He wrote: "Just as we can cool water below its freezing-point without completely freezing it, thereby rapidly increasing the strength with which the water tends to freeze, so by a relatively rapid cooling we can carry the metal considerably below Ar_1 without giving the Ar_1 change time to proceed far, strengthening the while the tendency toward this change, which keeps kindling more

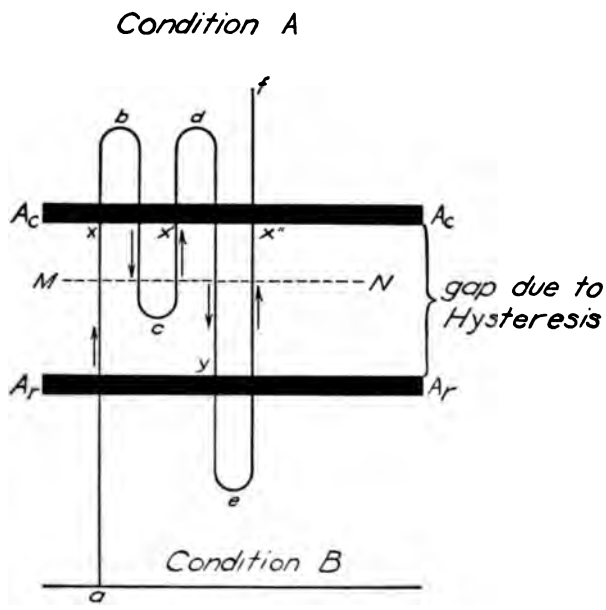

Fig. 1. — Diagram showing reversible critical point.

and more till it bursts into a blaze, with such evolution of heat as actually to recalesce, to raise the temperature of the metal by some 10 deg., in spite of the continued abstraction of heat by the continued cooling of the furnace."

The slower the heating and cooling the nearer will the two points approach each other, so that with infinitely slow cooling and heating they would undoubtedly occur at exactly the same temperature. If there remained any doubt as to the points Ac_1 and Ar_1 representing the opposite phases of the same phenomenon, i.e. of A being a reversible point, it would suffice to dispel it to consider the fact that in order to induce the retardation Ar_1 the steel must first be heated *past* the point Ac_1; and reciprocally the retardation Ac_1 cannot take place unless the metal has first been cooled to a point below Ar_1. To illustrate: the melting of ice and the freezing of water are undoubtedly the opposite phases of the same phenomenon, each one undoes the work of the other, and in order to freeze the water we must first melt the ice and likewise to melt the ice the water must first be frozen; one change cannot be induced unless the opposite one has last taken place. Indeed it is possible through very slow

and undisturbed cooling to lower the temperature of water below its freezing-point before it starts freezing, a clear instance of hysteresis, although in this case called "surfusion," and when freezing takes place the temperature of the water *rises* to its normal freezing-point, a clear case of recalescence although deprived of glow.

The diagram shown in Figure 1 illustrates further this reversibility of the point A_1. Let two parallel lines represent the phases Ac and Ar of the critical point. Let condition *A* represent the state of the metal stable above Ac and condition *B* the state of the metal stable below Ar. The gap between Ac and Ar is due to hysteresis. *MN* is the temperature at which both the Ac point and the Ar point would occur if there was no hysteresis as, for instance, if the metal could be heated and cooled infinitely slowly. Assuming the metal to be in condition *B* at *a*, below Ar, on heating it from *a* to *b* above Ac on reaching the Ac point at *x* it passes from the condition *B* to the condition *A* with absorption of heat causing a retardation in the heating; on cooling from *b* to *c*, that is to a temperature below Ac but above Ar, the condition *A* is retained so that upon heating from *c* to *d* no transformation can take place at *x'* on passing through the Ac point and therefore no critical point observed. If the metal be cooled from *d* to *e*, however, on passing through Ar at *y* it changes from condition *A* to condition *B* with evolution of heat, causing a retardation in the rate of cooling; if it now be heated again from *e* to *f* above Ac, a critical point will be observed at *x''* since the metal now in condition *B* will pass to condition *A*.

It will be evident that between Ar and Ac the metal may be in condition *A* or condition *B* depending upon whether it was last cooled from above Ac or heated from below Ar.

Speed of Cooling and Heating vs. Position of A_1. — It has been seen that the faster the cooling the lower is the position of the point Ar_1 and the faster the heating the higher the point Ac_1, that is, the faster the cooling and heating the greater the gap between the opposite phases Ar_1 and Ac_1 of the reversible point A_1.

The cooling of a piece of steel may be so rapid, as in quenching, as to prevent altogether the retardation Ar_1 from taking place, because a low temperature is so quickly reached that the rigidity of the metal prevents the transformation of which Ar_1 is a manifestation. In other words time and a certain amount of plasticity are required for the transformation Ar_1 to occur, and in quenching time is denied when the metal is sufficiently plastic (i.e. at a red heat), while when time is given (i.e. after quenching) the metal has lost its plasticity. It remains untransformed or but partially transformed. It will be shown in another lesson that this suppression of the point Ar_1 is probably the cause of the hardening of carbon steel by sudden cooling.[1]

Le Chatelier rightly reminds us that the speed of the transformations occurring at the critical points of steel follows the general laws which govern the speed of all chemical phenomena. In other words that the speed of the transformation is the greater (1) the higher the absolute temperature and (2) the wider the range between the actual temperature and the temperature of equilibrium, that is the temperature at which the transformation is due. Above the critical temperature both influences act in the same direction and the speed of transformation increases without limit. Below the critical temperature these influences act in opposite directions necessarily giving rise to the existence of a maximum speed. According to Le Chatelier this notion of variable speeds of transformation accounts for all the peculiarities of the

[1] It will be explained later that some writers have doubted the suppression of the transformations on rapid cooling and have suggested another explanation of the hardening of steel.

hardening treatment. On heating it is hardly possible to raise the temperature of transformation more than 100 deg. C. through very rapid heating, while during cooling the speed reaches its maximum at about 600 deg. C., is very feeble below 200, and nearly null at atmospheric temperature.

Chemical Composition vs. Position of A_1. — Generally speaking impurities have a tendency to lower the position of Ac_1 and Ar_1, some of them decidedly. Osmond, for instance, indicates the position of Ar_1 in a steel containing 1 per cent of Mn as 685 deg. whereas with 4 per cent of manganese the same point was lowered to 590 deg. It is conceivable that further increase of that element must lower still more the critical point, so that finally it may be lowered below atmospheric temperature, being apparently eliminated. It will be shown in another lesson that this is precisely what occurs in the cases of manganese steel and high nickel steel, containing respectively some 13 per cent of manganese or some 25 per cent of nickel. These steels exhibit no retardation on cooling from a high temperature to atmospheric temperature. When cooled to lower temperatures, however, by immersing them in freezing mixtures, or, if need be, in liquid air, the retardations may again occur. In the case of commercial steel of good quality the proportion of impurities, with the possible exception of manganese, varies within relatively very narrow limits, so that no great variation should be expected in the position of the critical point A_1. Neither is it clear that the amount of carbon present in steel has a marked effect upon the position of the point A_1, although some writers state that the point is lifted as the carbon increases. The point Ar_1 almost invariably occurs somewhere between 650 and 700 deg. C. and its reversal Ac_1 25 to 50 deg. higher. Both Ar_1 and Ac_1 would probably occur at about 710 deg. could the cooling and heating be infinitely slow.

Upper Critical Points. — The existence of upper critical points, that is of thermal retardations occurring at temperatures higher than that of the recalescence point, has already been alluded to. These points were discovered by Osmond and their discovery ushered in a new epoch in the scientific study of iron and steel. To describe these points it is advisable to consider first the thermal retardations occurring in cooling and heating carbonless iron and then similar retardations exhibited by steel containing increasing amounts of carbon.

Thermal Critical Points in Pure Iron. — On cooling from a high temperature, say 1000 deg. C., a piece of the purest iron obtainable and ascertaining its rate of cooling as previously explained, the metal is found to cool normally, i.e. at a uniformly retarded rate, until a temperature of some 900 to 850 deg. C. is reached when a marked retardation is observed in the rate of cooling, indicating a spontaneous evolution of heat, in this case, however, insufficient to cause an actual rise of temperature, i.e. a recalescence of the metal. The cooling then resumes, or nearly resumes, a normal rate of cooling, until at about 750 deg. C. a second evolution of heat takes place causing another retardation in the rate of cooling, not so marked, however, nor so sharply defined as the first one. The metal then cools normally or quite so to atmospheric temperature. We have thus detected two unmistakeable spontaneous evolutions of heat in the cooling of pure iron. The corresponding critical points are called Ar_1 and Ar_2, the latter symbol indicating the lower point. It should be noted that the recalescence point which should occur at some 675 deg. is here absent. Carbonless iron has no point of recalescence.

These two upper points like the point of recalescence are reversible critical points, i.e. on heating the opposite phases of the transformations (whatever those trans-

formations may be) take place with absorption of heat, causing a retardation in the rate of heating and the corresponding points being designated by the symbols Ac_3 and Ac_2. The point Ac_3 occurs at a temperature some 20 to 30 deg. higher than its reversal Ar_3, while Ac_2 occurs at nearly the same temperature as Ar_2.

Thermal Critical Points in Very Low Carbon Steel. — Let us now take a sample of steel containing some 0.10 per cent carbon, and let us ascertain its rate of cooling from a high temperature precisely as before. Three thermal retardations will be detected, Ar_3 at about 850 deg., Ar_2 near 750 deg., and Ar_1 (point of recalescence) near 675 deg. Of these three spontaneous evolutions of heat the upper one at Ar_3 will be the most marked, while at Ar_2 and at Ar_1 they will be quite faint, their satisfactory detection calling for the use of delicate instruments and careful manipulations. On heating corresponding retardations will occur, due to spontaneous absorptions of heat, the resulting critical points being designated as Ac_3, Ac_2, and Ac_1. Of these Ac_3 and Ac_1 will occur at temperatures some 25 deg. or more higher than Ar_3 and Ar_1 while Ac_2 will occupy nearly the same position as Ar_2 on the temperature scale, that is about 750 deg.

Peculiarities of the Point A_2. — The point A_2 is generally less marked than the points A_3 and A_1. Unlike A_3 its position is little affected by the carbon content, and unlike A_3 and A_1 the point on heating, Ac_2, occurs at nearly the same temperature as the point on cooling, Ar_2. To these peculiarities must be added another one, namely the fact that A_2 appears to cover a wide range of temperature. While its intensity decreases with fall of temperature its lower limit probably extends to considerably below 700 deg. In other words the transformation of which A_2 is a manifestation is not completed by the time the point A_1 is reached. Indeed Osmond mentions 550 deg. C. as the probable lower limit of the point A_2. Some explanations of these peculiarities of the point A_2 will soon be offered.

Thermal Critical Points of Medium High Carbon Steel. — The determination of the rate of cooling of a steel containing some 0.45 per cent carbon reveals the existence of two critical points, one, evidently the point of recalescence, Ar_1, at the usual temperature (650 to 700 deg.) and one upper point in the vicinity of 725 deg. Does the presence in this steel of only one upper point mean that one of the two upper points detected in carbonless iron and in very low carbon steel has disappeared because of the presence of more carbon, or does it mean that the two upper points have now united into a single one? The latter view is generally assumed to be the correct one and this single upper point of medium high carbon steel is designated accordingly by $Ar_{3.2}$. This notation clearly implies that the two distinct evolutions of heat which in carbonless iron and in very soft steel occur separately at Ar_3 and Ar_2 here occur at one and the same temperature. Increasing the carbon content decreases the interval of temperature between the two upper points until, finally, for a certain carbon content the points meet to form the double point $Ar_{3.2}$.

Merging of A_3 and A_2. — It has been seen that as the carbon increases the point A_3 is gradually lowered until finally it merges with A_2, whose position is not greatly affected by the presence of carbon, to form the point $A_{3.2}$. It would be interesting to know the exact proportion of carbon required to cause this merging. This, however, is difficult to ascertain because of the experimental difficulty of separating two critical points situated very near each other as they must be in the vicinity of the merging point, and also because this merging will be shifted somewhat by speed of heating and cooling and by slight changes of chemical composition. From the mass of experi

mental evidences which has been published it seems probable that the merging takes place at about 0.30 per cent carbon.

Thermal Critical Point in Eutectoid Steel. — Eutectoid steel, that is steel containing some 0.85 per cent of carbon, exhibits but one critical point, the point of recalescence, very marked at about 675 deg. C. on cooling. Shall it be inferred from the occurrence of this single point that in eutectoid steel the transformations of which the upper points A_3 and A_2 or the double point $A_{3.2}$ are manifestations do not take place? Or shall it be assumed that these transformations now take place at the same temperature as the transformation corresponding to the critical point A_1? In other words that increasing the amount of carbon has so depressed the position of the two upper points as to cause them to unite with the lower point, forming now a triple point to be designated as $Ar_{3.2.1}$? This is the view generally held. The critical point on heating is designated by the notation $Ac_{3.2.1}$. It will be explained in another lesson why the points A_3, A_2, or $A_{3.2}$ cannot exist in eutectoid or hyper-eutectoid steel, when it will also be shown that the single point of eutectoid steel is not in fact a merging of A_3, A_2, and A_1, but merely the point A_1, the upper points having disappeared.

Merging of $A_{3.2}$ and A_1. — As the carbon content of the steel increases still more after the merging of A_3 and A_2 has been effected, the interval between the points $A_{3.2}$ and A_1 gradually diminishes until these two points, in turn, appear to merge to form the triple point $A_{3.2.1}$. Theoretically this apparent merging should occur when the steel is composed entirely of pearlite, that is, when it contains in the vicinity of 0.85 per cent carbon, for reasons that will later be made clear. As a matter of fact, however, the merging seems to take place long before so large a proportion of carbon is present, for the point $A_{3.2}$ is seldom detected in steel containing more than some 0.50 or 0.60 per cent of carbon; this is probably due, as already explained, to the difficulty of separating, experimentally, two critical points so close to each other.

Thermal Critical Points in Hyper-Eutectoid Steel. — Carefully conducted observations reveal the existence of an upper critical point in hyper-eutectoid steel, at least in steel containing a decided amount of free cementite, and, of course, of the point of recalescence. It seems proper to designate this upper point by the symbol A_{cm} (Ar_{cm} on cooling, Ac_{cm} on heating) for reasons later to be given, cm standing for cementite. At least one writer, however, has designated this point on cooling by the notation Ar_{mc}, mc standing for massive cementite. Other writers have called it an A_3 point, a notation from which one would naturally infer that this upper point of hyper-eutectoid steel is similar to the upper point of iron and of very low carbon steel, which is not the case.

Purely theoretical considerations lead us to infer that the position of the point A_{cm} is lowered as the proportion of carbon decreases, finally merging with the point $A_{3.2.1}$ at the eutectoid point. It would follow from this that the single point of eutectoid steel is really a merging of four points A_3, A_2, A_1, and A_{cm} and that it should accordingly be designated by $A_{3.2.1\ cm}$. It is, however, the universal custom to ignore this contribution of A_{cm} to the single point of eutectoid steel and to use for the latter the notation $A_{3.2.1}$.

The amount of heat evolved at Ar_{cm} is very slight, hence the difficulty of detecting this point. Carpenter and Keeling ascertained its existence in steels containing respectively 1.31, 1.51, 1.69, 1.85, and 1.97 per cent carbon at the following corresponding temperatures: 883, 911, 985, 1030, and 1042 deg. C. With lower carbon

contents, that is nearer the eutectoid composition, the heat evolved is so slight that the detection of Ar_{cm} as a separate point is quite impossible. In theoretical diagrams, however, the existence of this point is always indicated in all hyper-eutectoid steels with a sharp merging with $A_{3.2.1}$ at the eutectoid point.

The point Ar_{cm} then should occur in all hyper-eutectoid steels at temperatures increasing from some 700 to 1050 deg. C. as the carbon increases from 0.85 to 2.0 per cent.

Merging of $A_{3.2.1}$ and A_{cm}. — As already explained theoretically the merging of the points $A_{3.2.1}$ and A_{cm} should take place at the eutectoid composition, that is, for steel containing in the vicinity of 0.85 per cent carbon. Experimentally, however the point A_{cm} cannot be detected in steel containing less than some 1.20 per cent carbon. Bearing in mind that hypo-eutectoid steels containing more than 0.60 per cent carbon or thereabout have likewise but one critical point so far as experimental evidences are concerned, it will be seen that for all practical purposes we may consider all grades of steel containing from 0.60 to 1.20 per cent carbon as having but one critical point, namely, the point of recalescence, at some 675 deg. C. on cooling although theoretically eutectoid steel only should have but one such point.

Minor Critical Points. — Some experimenters believe to have discovered some critical points other than those so far described. These points, which may be referred to as minor critical points correspond to very faint evolutions or absorptions of heat, and produce, therefore, but very slight jogs in the thermal curves. Their existence is not fully established and they appear to have but little if any influence upon the practical side of our subject. They should, however, be mentioned in these lessons so that the student may at least have some idea of their nature and claims to recognition. Roberts-Austen in 1898 detected a slight evolution of heat between 550 and 600 on cooling iron and hypo-eutectoid steel, and this point was again detected by Carpenter and Keeling in 1904. The latter observers named it the Ar_5 point, following in this Roberts-Austen.

Roberts-Austen detected another evolution of heat in pure iron between 450 and 500 deg. the existence of which he ascribed to the presence of hydrogen resulting in a separation of hydroxide of iron taking place at this critical point. Finally the same observer described one more slight evolution of heat in pure iron at about 270 deg. C. which he tentatively ascribed to the formation of an iron-iron hydroxide eutectic.

Arnold believes in the existence of a critical point between A_3 and A_2, of maximum intensity when the steel contains some 50 per cent of pearlite (about 0.45 per cent carbon) which he thinks due to the formation or segregation of pearlite and hardenite, a constituent later to be described.

Data Showing the Position of the Critical Points. — By far the most comprehensive set of determinations of the critical points of iron and steel was made by Carpenter and Keeling. Their results are shown in the table on the following page. The table includes the critical points occurring during the solidification period of the various steels and irons investigated. These will be considered in another lesson.

Relative Quantities of Heat Evolved or Absorbed at the Critical Points. — The various critical points that have been considered in the preceding pages do not indicate evolutions or absorptions of equal quantities of heat; they are not of equal intensity. The point A_3 is very marked and sharply defined in carbonless iron but decreases rapidly in intensity as the carbon increases. The point A_2 is relatively feeble and not very sharply defined and as already mentioned shows a tendency to cover a considerable range of temperature. Its intensity moreover is little affected by the carbon content of the steel. The point $A_{3.2}$, being a merging of A_3 and A_2, is more intense than A_2 but less intense than A_3 in carbonless iron owing to the fact that when the merging takes place the A_3 point has lost much of its intensity. The

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	
Alloy No.	Carbon per Cent.	Range of Solidification.		Ar.m.c.	Ar3		Ar2.		Ar1.		Ar0.	Alloy No.
		Beginning.	End.	Beginning.	Beginning.	Maximum.	Beginning.	Maximum.	Beginning.	Maximum.	Beginning	
1	0·01	...	...	...	901	900	784	762	...	...	616	1
2	0·02	1504*	1470*	...	900	890	795	762	...	...	600	2
3	0·05	...	...	...	905	884	780	762	...	...	...	3
4	0·12	1504†	1470†	...	894	838	774	762	693	688	600	4
5	0·16	1498†	1465†	...	872	837	771	762	697	693	576	5
6	0·17	1497†	1450†	...	...	...	...	...	...	...	...	6
7	0·24	1492†	1448†	...	890	Merged	...	762	696	693	611	7
8	0·38	1479†	1416†	...	...	...	778	762	700	699	...	8
9	0·47	1482†		...	...	...	777	762	...	703	587	9
10	0·53	1473†	1404†	...	...	...	762	730	...	700	617	10
11	0·61	1469†	1394†	...	...	...	780	Merged	Merged	699	593	11
12	0·80	1457‡	1351‡	...	...	...	...	...	...	(704)	...	12
13	0·80	1454†	...	...	...	...	...	...	...	(695)	...	13
14	0·81	1460†	1351†	...	774	Merged	...	Merged	Merged	706 (705)	...	14
15	0 93	1443†	...	...	774	,,	...	,,	,,	699	587	15
16	1·31	1426†	1286†	883	774	,,	...	,,	,,	(711) 695	600	16
17	1·51	1406†	1244†	911	768	,,	...	,,	,,	(713) 684	587	17
18	1·69	1388†	...	985	774	,,	...	...	...	(708) 710	...	18
19	1·81	1383†	...	...	...	...	...	...	...	...	...	19
20	1·85	1383†	1179†	(1015) 1030	783	Merged	...	Merged	Merged	(711) 711	...	20
21	1·97	1367†	...	(1042)	...	...	...	...	...	(710)	...	21
22	2·12	1350†	1110†	...	...	...	...	...	...	(714)	...	22
23	2·21	1354†	1107†	...	801	Merged	...	Merged	Merged	714	610	23
24	2·25	1352†	1122†	...	...	...	...	...	...	...	...	24
25	2·25	1348†	1122†	...	...	...	...	...	...	(714)	...	25
26	2·47	1330†	1134†	1035	801	Merged	...	Merged	Merged	708	622	26
27	2·63	1305†	...	1040	801	...	...	...	...	716	610	27
28	2·67	1306†	...	...	...	...	...	...	...	...	...	28
29	2·74	1300†	1139†	...	...	...	...	...	...	...	...	29
30	2·85	1292†	1139†	1058	...	Merged	...	Merged	Merged	716 (715)	613	30
31	3·03	1277†	1139†	...	777	,,	...	,,	,,	702 (717)	610	31
32	3·29	...	1141†	...	...	...	...	...	...	...	...	32
33	3·42	1238†	1114†	1058	790	Merged	...	Merged	Merged	703 (714)	610	33
34	3·51	1230†	1136†	...	...	...	...	...	...	...	...	34
35	3·87	1190†	1144†	1090	770	Merged	...	Merged	Merged	(716) 716	600	35
36	3·98	1171*	1138*	1087	...	...	...	...	...	713	604	36
37	4·37	1136*	1136*	...	...	...	...	...	...	(714)	...	37
38	4·50	1146*	1146*	1087	777	Merged	...	Merged	Merged	715	616	38

* Thermojunction M_3 platinum platinum 10 per cent. iridium.
† ,, M_5 ,, ,, ,, ,,
‡ ,, M_4 ,, ,, ,, rhodium.

The temperatures in brackets in columns 5 and 11 were obtained by direct cooling. All other temperatures in columns 5–12 were obtained by differential cooling.

Ar.m.c. represents separation of massive cementite.
Ar3 ,, change from γ to β iron.
Ar2 ,, ,, ,, β to α ,,
Ar1 ,, ,, ,, hardening carbon to pearlite carbon.
Ar0

point A_1 is feeble in very low carbon steel but its intensity increases rapidly with the carbon content, becoming so great as to cause the metal to glow or recalesce as previously described and being maximum for steel of eutectoid composition. These differences in the thermal values of the critical points will be explained in another lesson.

Graphical Representation of the Position and Magnitude of the Critical Points. — The position of the critical points corresponding to various percentages of carbon is illustrated graphically in Figure 2. The diagram refers to the critical points of cooling, i.e. the Ar points, and it should be borne in mind that the corresponding points on heating, the Ac points, occur some 25 to 50 deg. higher, with the exception of the point Ac_2 which seems to occupy nearly the same position as the point Ar_2. An attempt has been made in this diagram to indicate the relative intensities of the various points by shaded areas of proportional thickness on both sides of the lines indicating their position. This is based chiefly on theoretical considerations and is in accordance with the generally accepted views regarding the causes of the critical points as explained in the next lesson. An examination of the diagram shows (1) that the point Ar_3 intense in carbonless iron decreases gradually in intensity as the carbon increases, (2) that the intensity of Ar_2 is not greatly affected by the carbon content, (3) that $Ar_{3.2}$ fairly intense at first becomes rapidly feebler and finally disappears just as it meets Ar_1, (4) that Ar_1 at first very faint becomes more marked with increased carbon, being maximum for a carbon content of some 0.85 per cent (the eutectoid point), (5) that the point $Ar_{3.2.1}$ very intense at the eutectoid point gradually loses some of its intensity, although always remaining pronounced, and (6) that the point Ar_{cm} very faint near the eutectoid composition increases in intensity with the carbon content.

These theoretical inferences are well supported by experimental evidences in the case of the magnitude of the points Ar_1 and $Ar_{3.2.1}$ and quite satisfactorily in regard to Ar_3 and Ar_{cm}. They ascribed to the points Ar_2 and $Ar_{3.2}$, however, a magnitude and a sharpness which is not borne out by experiments as later explained when it will also be seen that some writers doubt the accuracy of the explanation generally offered to account for the point A_2.

The diagram, therefore, while undoubtedly useful, is probably but approximately accurate and likely to be modified with increased knowledge of the facts it aims to depict.

Determination of the Thermal Critical Points. — The thermal critical points are universally determined by means of the Le Chatelier thermo-electric pyrometer. Indeed it is the invention of this invaluable instrument that made the detection of the upper critical points possible. Had it not been invented we probably would still be in ignorance of the existence of the upper points, while we would have but little knowledge of the exact position of the point of recalescence. The necessary experimental manipulations will be found described in the instructions given to carry on the experiments appended to this lesson.

Cooling and Heating Curves. — The determination of the thermal critical points calls for the construction of heating and cooling curves. In these curves successive falls (or rises) of temperature, say of 10 deg. C., $\theta - 10, \theta - 20, \theta - 30 \ldots$ are plotted as ordinates, while as abscissæ are plotted (*a*) the corresponding time intervals in seconds, t, t′, t″, t‴ . . . elapsed since the beginning of the observation, or (*b*) the actual intervals of time $t' - t$, $t'' - t'$, $t''' - t'' \ldots$ required for each noted fall of

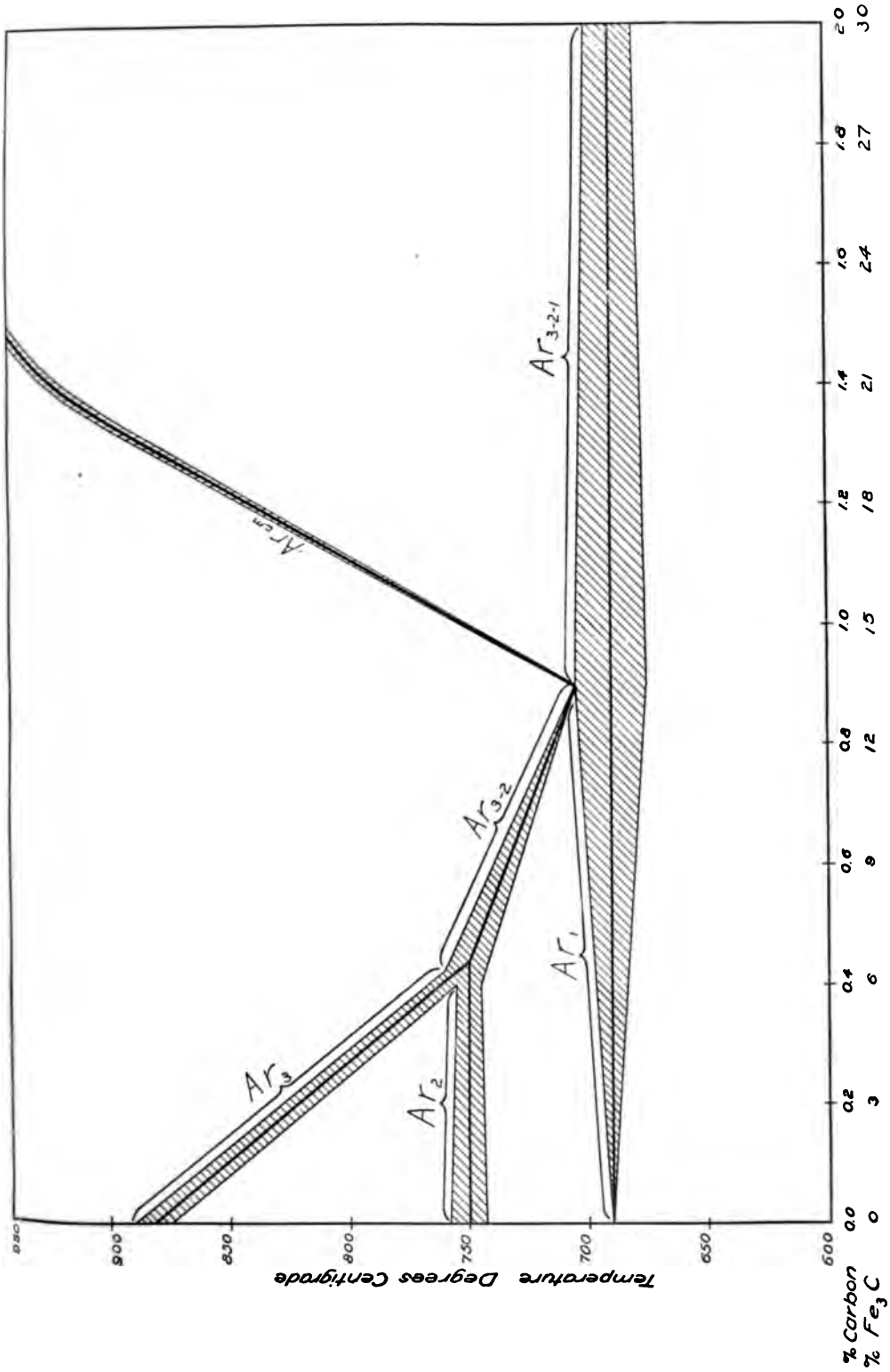

Fig. 2. — Diagram showing the position and magnitude of the critical points.

temperature. In other words the coordinates are θ and t in the first instance, θ and $\frac{dt}{d\theta}$ in the second. The curve obtained by the first method is known as a time-temperature curve while the second method yields an inverse rate curve.[1]

Time-temperature curves representing the heating and cooling of pure iron are shown in Figure 3. While in these curves the evolutions or absorptions of heat cor-

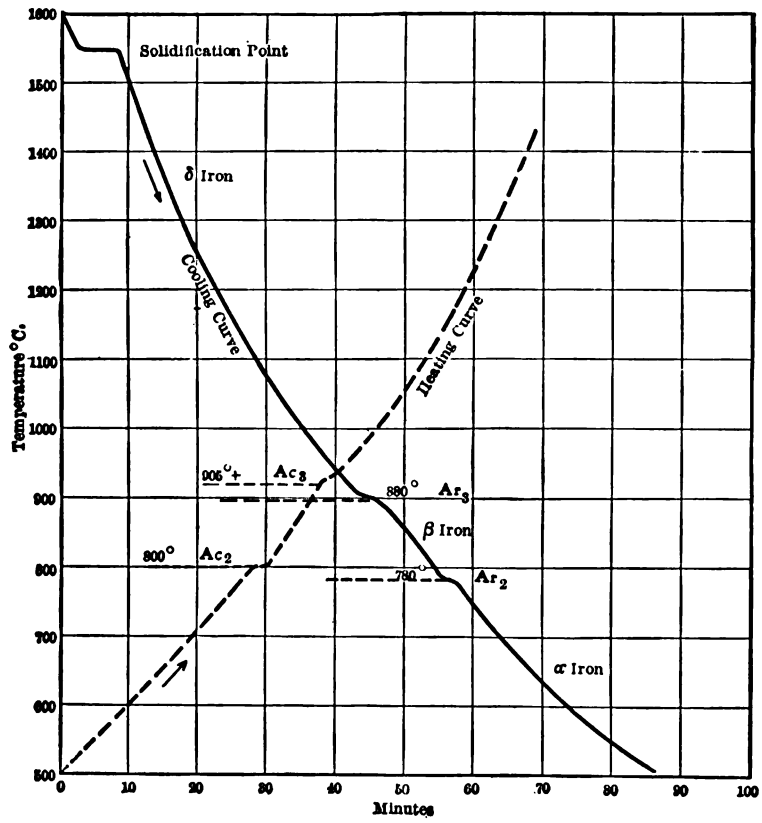

Fig. 3. — Time-temperature curves. Heating and cooling of pure iron. (Goerens.)

responding to the points A_3 and A_2 can be detected, they do not stand out very conspicuously, and it may well be feared that slight thermal retardations might escape detection in curves of this kind since they would cause but very slight jogs in the curve. These considerations led Osmond to adopt the inverse rate method for the plotting of thermal curves. Curves of this type are shown in Figures 4 and 5. The thermal points correspond to sharp peaks in the curves, the lengths of which are roughly proportional to the amount of heat evolved on cooling or absorbed on

[1] It is evident that similar curves would result from reversing the observations, i.e. noting the successive falls of temperatures θ, θ', θ'' . . . corresponding to equal intervals of time, say of 15 seconds, t + 15, t + 30, t + 45 . . . and plotting the former as ordinates and the latter as abscissæ. The coordinates in this case would be $\frac{d\theta}{dt}$ and t.

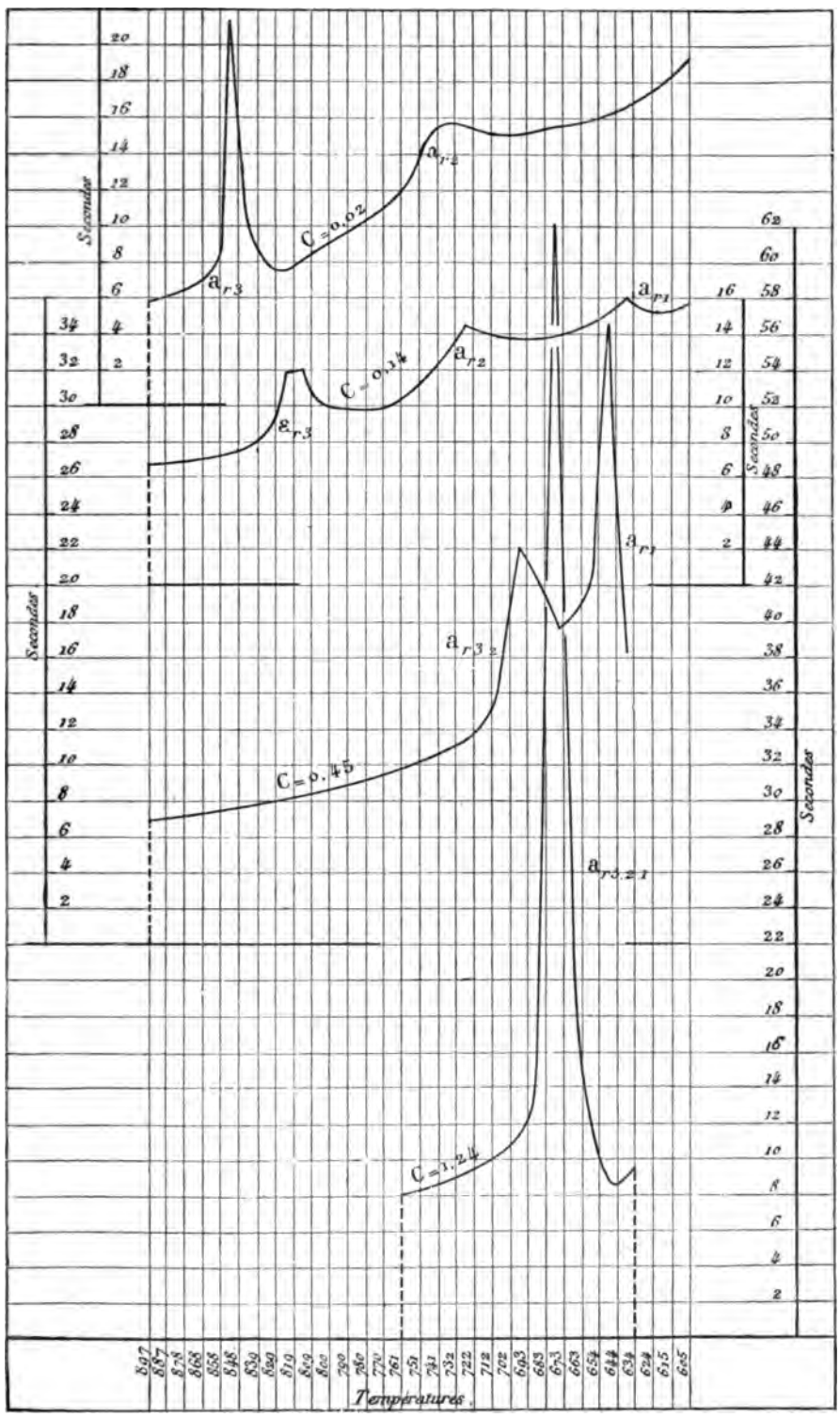

Fig. 4. — Inverse rate curves. Cooling of steels containing respectively 0.02, 0.14, 0.45, and 1.24 per cent carbon. (Osmond.)

heating. This method is quite universally applied unless, as later explained, a neutral body is used for the determination of the critical points.

Use of Neutral Bodies. — The method described above for the detection of the thermal critical points is open to the objection that the rate of cooling or heating of the steel under observation is necessarily affected by any irregularity in the cooling or heating of the furnace itself and by other outside agencies. These disturbing factors introduce irregularities in the thermal curves which may render their interpretation difficult and may indeed altogether hide the existence of critical points where but a very small amount of heat is evolved or absorbed. Again, on cooling for instance, when a critical point is reached the temperature of the metal is affected in opposite directions (1) by the cooling furnace which has a tendency to lower its tem-

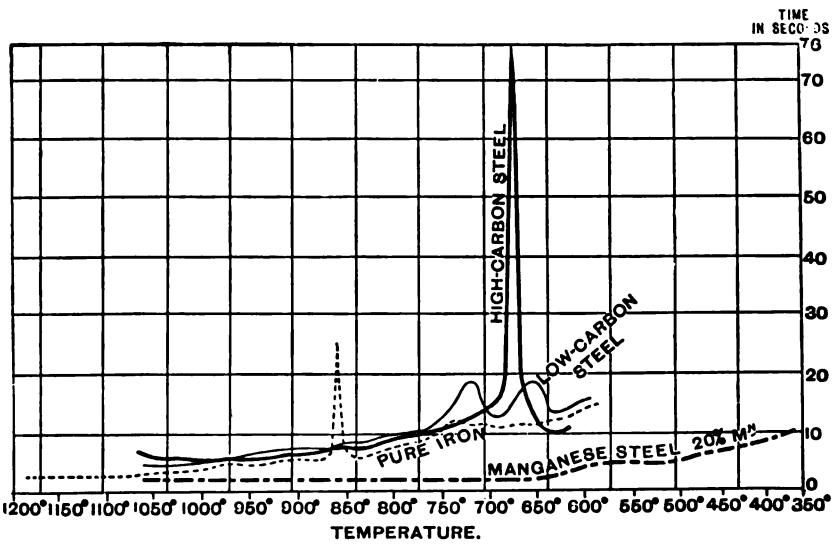

Fig. 5. — Inverse rate curves. Cooling of pure iron, low carbon steel, high carbon steel, and manganese steel. (Roberts-Austen.)

perature and (2) by the evolution of heat occurring at the critical point, the effect of which is to raise its temperature. It is evident that the cooling influence of the furnace has a tendency to decrease the apparent magnitude of the critical point and therefore to mask it.

The elimination of these objectionable influences should result in sharper thermal curves and in the detection of faint evolutions or absorptions of heat. This was accomplished by Roberts-Austen through the use of a neutral body and double thermocouple so connected that the difference of temperature between the metal under investigation and the neutral body is recorded, as well as the actual temperature of the metal.[1] If the heat capacities and emissivities of the metal and of the neutral piece were identical their temperature would be exactly the same except at the critical points, when heat is evolved or absorbed by the metal while the neutral body is, of

[1] For the arrangement of the galvanometers, connections, etc., see the description of the Saladin-Le Chatelier-Pellin instrument described under "Apparatus" and the description of other instruments using neutral bodies in an appendix to these lessons.

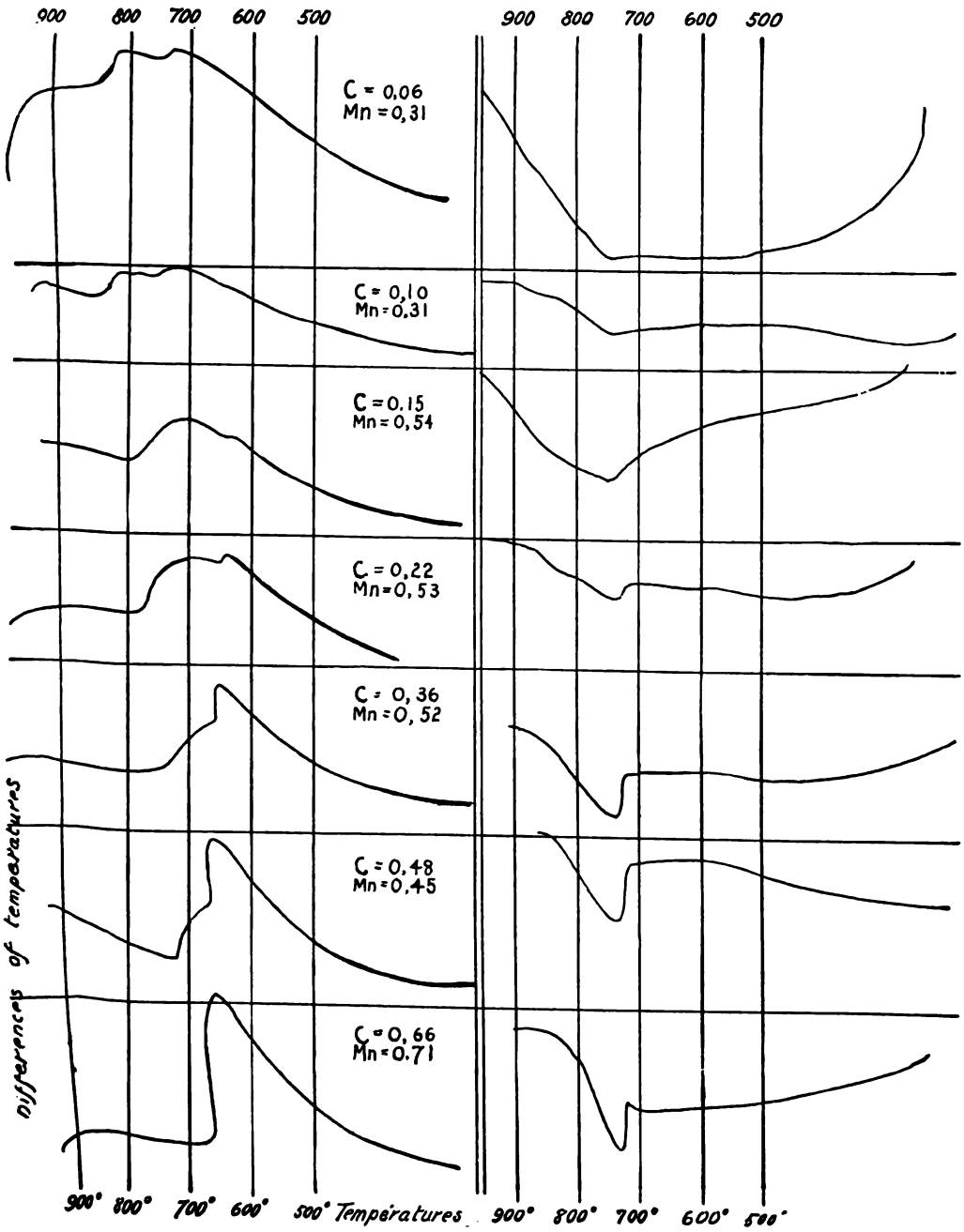

Fig. 6. — Difference curves. Cooling and heating of various steels. (Saladin.)

course, free from any such thermal disturbance. Any difference of temperature between the two pieces, therefore, would indicate a critical point. Since it is generally impossible, however, to use a neutral body having exactly the same heat capacity as that of the metal under observation, it will be apparent that there will always be a difference between the temperatures of the two pieces, one always lagging behind the

other, and that the critical points will correspond to sudden increase in the diff between their respective temperatures. Since, however, the critical points a caused solely by abrupt differences between the temperatures of the two bodie are freed from the irregularities mentioned above as well as from the mask fluence of the falling or rising temperature of the furnace, seeing that both pie now equally affected, and the curves obtained should indicate more sharply an spicuously the existence of even faint absorptions or evolutions of heat.

The neutral body should, of course, be free from any thermal transfor within the range of temperature covered by the experiments. Platinum, por clay, 25 per cent nickel steel, and (by the author) austenitic manganese stee been used. The plotting of the thermal curves when a neutral body is used n done in two different ways, (1) successive falls (or rises) $\theta - 10$, $\theta - 20$, $\theta - 30$ the temperature of the metal as indicated by one of the galvanometers may be

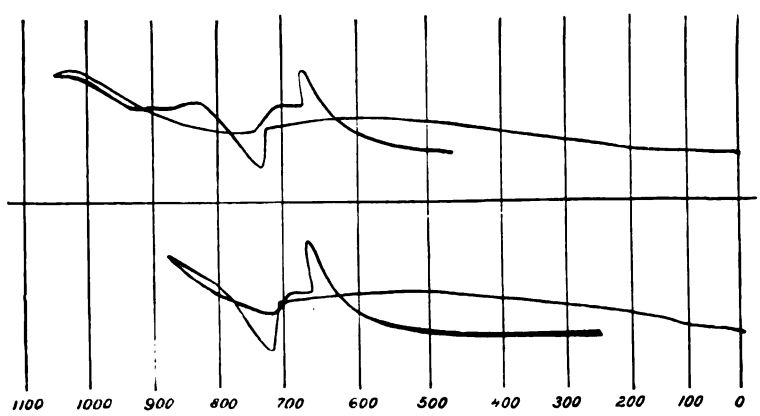

Fig. 7. — Difference curves. Cooling and heating curves taken on same photographic plate. (Saladin.)

as ordinates against the corresponding differences in temperature $\theta - \theta_1$, θ $\theta'' - \theta''_1$ . . . of the two cooling bodies, as indicated by the second galvan the coordinates in this case being θ and $\theta - \theta_1$, and the curve known as a "diffe curve, or (2) according to Rosenhain, successive falls of temperature may be as ordinates against the corresponding *rate of cooling for each degree of temp* $\frac{\theta - \theta_1}{\theta}, \frac{\theta' - \theta'_1}{\theta'}, \frac{\theta'' - \theta''_1}{\theta''}$ as abscissæ, the coordinates being in this method $\frac{d\,(\theta - \theta_1)}{d\,\theta}$ and the curve known as a "derived differential" curve.

Difference curves are shown in Figures 6, 7, and 8. The curves of Figures were taken with a Saladin-Le Chatelier-Pellin instrument. Figure 6 shows t ical points on heating and cooling of a series of carbon steels containing from 0.66 per cent carbon, the cooling and heating curves having been taken on s photographic plates. In Figure 7 is shown the heating and cooling curves ta the same plate of two steels containing respectively 0.36 and 0.46 per cent car

The curves of Figure 8 are difference curves of a series of very pure carbo taken by Carpenter and Keeling.

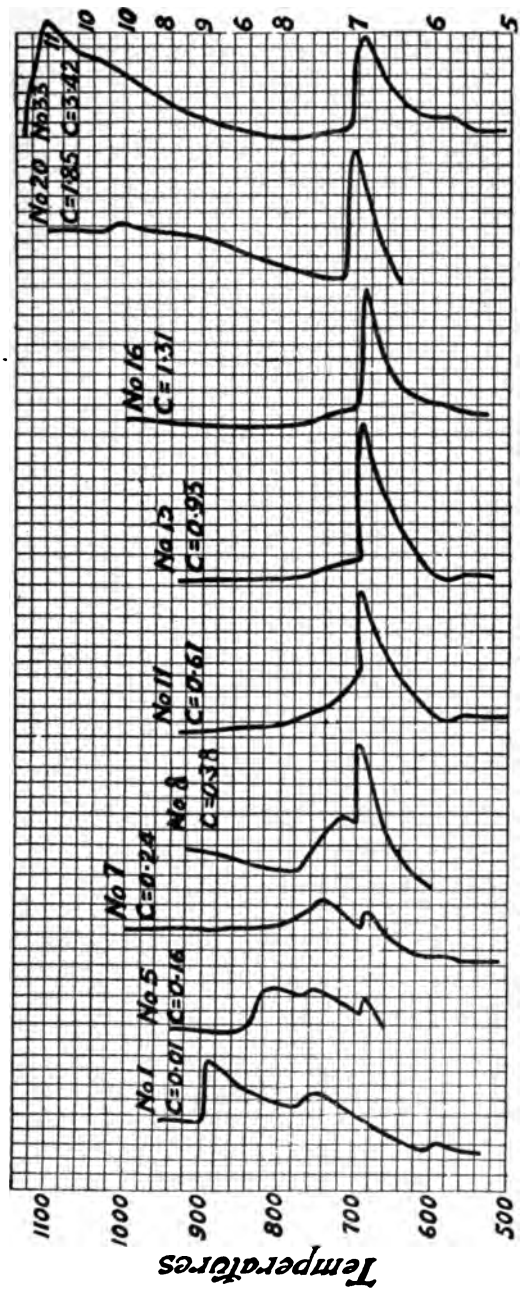

Fig. 8. — Difference curves. Cooling of a series of very pure carbon steels. (Carpenter and Keeling.)

The purpose of Rosenhain's derived differential method of plotting is to eliminate the irregularities from which difference curves still suffer and which are due chiefly to differences between the heat capacities and emissivities of the sample and neutral body resulting in differences in their rates of cooling and heating. The resulting

curves cannot, of course, be autographically recorded. They call for the replot of the data afforded by the difference (θ vs. $\theta - \theta_1$) curves.

Additional Illustrations of Cooling Curves. — The different types of cooling cu described in the preceding pages are well illustrated in Figure 9. These curves ı constructed from the data given in the following table, in which each unit in t re sents intervals of time of 15 seconds, θ the corresponding temperatures of the san and $\theta - \theta_1$ corresponding differences of temperature between the sample and a neu body cooling under identical conditions. The curve *B*, representing the cooling ci of a neutral body free from critical transformations, has been added for comparis

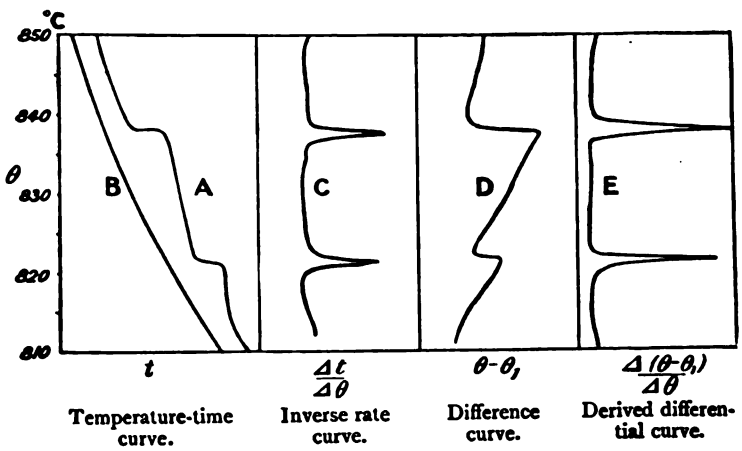

Fig. 9. — Different types of cooling curves. (Desch.)

t	θ	$\theta-\theta_1$	t	θ	$\theta-\theta_1$
5	850.0°	8.5°	18	829.0°	11.0°
6	848.0	8.5	19	825.0	8.2
7	844.7	7.5	19.5	823.3	7.3
8	842.0	7.0	20	822.2	6.7
9	839.5	6.3	21	821.7	7.7
10	838.5	7.0	22	821.5	8.5
11	838.2	8.8	23	821.3	9.8
12	838.1	10.2	24	821.1	10.1
13	838.0	12.0	24.5	819.0	9.5
14	837.9	13.6	25	815.0	6.0
15	837.5	15.5	26	813.0	5.0
16	836.0	14.6	27	811.6	4.7
17	833.0	13.0			

Self-Recording Pyrometers. — With the use of neutral bodies self-recording struments are generally employed. The Saladin-Le Chatelier-Pellin autogra pyrometer has been described under "Apparatus" and other types of self-recor instruments will be found described and illustrated in an appendix to these less The self-recording may be by means of photographic plates or by some other mecl ical devices. The former method calls for the use of mirror galvanometers sendi

beam of light upon the photographic plate while in other autographic recorders needle galvanometers are used. The relative merits between photographic recorders and other types are summed up by Burgess as follows:

"It is evidently of great advantage to use self-recording apparatus when possible, and it then becomes necessary to choose between the photographic type and the autographic. The latter possesses the advantage that the experimenter may watch any part of the record, and can therefore control the operation and at any moment vary the conditions affecting the experiment; whereas with a photographic recording apparatus, as usually constructed, the observer does not know whether or not the experiment is progressing properly until it is finished and he has developed the sensitive plate. The manipulation by the photographic method is usually also more delicate and time consuming and the adjustment less sure, and the record often requires further graphical interpretation. The autographic method is in general not adapted for interpreting phenomena taking place within an interval of a few seconds, so that for very rapid cooling it is necessary to employ the photographic method. It is possible to construct the photographic recorder so as to obtain a very considerable range of speeds with the same apparatus, while it is difficult and costly to construct an autographic recorder having more than two speeds."

Historical. — A brief historical sketch of the discovery of the critical points of iron and steel will not be without interest. In 1868 Tschernoff in studying the hardening of steel used the notation A for the temperature at which hardening by rapid cooling becomes suddenly possible in high carbon steel. This was the point $A_{3.2.1}$.

In 1869 Gore noted that at a dark red heat steel exhibited on cooling a spontaneous dilatation of short duration followed by normal contraction. Evidently the point of recalescence Ar_1 or $Ar_{3.2.1}$.

In 1873 Barrett repeated Gore's experiments and discovered, on heating, a momentary contraction at nearly the same temperature as the dilatation on cooling. This was the point Ac_1 or $Ac_{3.2.1}$. He further noted that this dilatation or contraction was very feeble in iron (the A_1 point in very low carbon steel) and very marked in hard steel (the point $A_{3.2.1}$). Barrett also discovered the spontaneous glow taking place on cooling a wire and gave it the name of recalescence.

In 1879 Barrus showed that the increase of hardness resulting from quenching was not gradual but sudden, thus pointing to the existence of a thermal critical point (the A_1 point).

In 1885 Osmond published his discovery of the upper critical points A_3 and A_2 in iron and low carbon steel and gave the first accurate determination of the position of the point A_1.

Experiments

Small samples of steel should be obtained containing respectively some 0.10, 0.25, 0.50, 0.85, and 1.50 per cent of carbon, preferably ½ in. round or square and 1 in. long. A small hole, about ⅛ in. in diameter, should be drilled in the end of each sample and extended to the center or even right through the sample. The end of the thermo-couple of a Le Chatelier pyrometer should be inserted in these small holes and firmly packed with loose asbestos. The sample thus attached to the thermo-couple should now be introduced in a suitable furnace, preferably an electric resistance furnace (see "Apparatus") and gradually heated to a temperature of some

1000 deg. C. While the metal is thus being heated its temperature should be obs and the time intervals required for each rise of temperature of say 10 deg. fully recorded. In a similar way the rate of cooling should be noted while the cools from 1000 to 500 deg. Inverse rate curves should be constructed whic bring out the evolutions or absorptions of heat having taken place durin thermal treatment. The accuracy of the method greatly depends upon the and skill exercised. The experiment calls for the services of two observers in that one may watch the galvanometer while the other notes and records the sponding times.

There is no difficulty by this method in detecting the points A_1 of medium c steel and $A_{3.2.1}$ of high carbon steel because very marked retardations occur at points. The detection of the points A_3 and A_2 and especially A_{cm}, where but evolutions of heat are involved, on the contrary is not always possible by method, their satisfactory detection calling for the use of neutral bodies and recording instruments. The same samples may be used.

Examination

I. Describe the occurrence of the thermal critical points in a steel containing per cent carbon.

II. Construct the inverse rate cooling curve of a piece of steel whose cooling thr successive ranges of 10 deg. C. has required the time intervals indicate low:

Temperatures Deg. C.	Time Seconds
750—740	10
40—30	11
30—20	12
20—10	13
710—700	14
700—690	16
90—80	20
80—70	45
70—60	20
60—50	17
50—40	15
40—30	16
30—20	18
20—10	20
610—600	23

III. Describe the influence of the rate of heating and cooling upon the positi the critical points.

IV. Explain why the points Ac_3 and Ar_3 do not correspond to the same tempera

V. Explain the use of neutral bodies in the determination of critical points b pyrometric method.

LESSON VIII

THE THERMAL CRITICAL POINTS OF STEEL

THEIR CAUSES

The thermal critical points described in the preceding lesson are evidently outward manifestations of internal transformations taking place spontaneously at certain critical temperatures. We should now inquire into the nature of these transformations.

Let us remember that there are but three well-known causes of spontaneous evolutions of heat in cooling bodies and of spontaneous absorptions on heating. These are: (1) formation of chemical compounds, a phenomenon which is almost always accompanied by a spontaneous evolution of heat (the heat of formation), and the reverse phase, the dissociation of the compound with absorption of heat (the heat of dissociation), (2) changes of state, that is, the passage of a substance from the solid to the liquid or from the liquid to the gaseous state, or directly from the solid to the gaseous state, which changes are always accompanied by spontaneous absorptions of heat, and the opposite phases of the same phenomena, the passage of a body from the gaseous to the liquid or from the liquid to the solid state, when heat is evolved (the latent heat of solidification in case of a substance passing from the liquid to the solid state, etc.) these evolutions or absorptions of heat, as the case may be, maintaining the temperature of the substance constant while a change of state is in progress as, for instance, during solidification or melting, (3) allotropic or polymorphic transformations which are always accompanied by an evolution of heat when the body passes from one allotropic condition to another, and by an absorption of heat when it returns to its first allotropic form or vice versa. The meaning of allotropy has been explained in Lesson II.

Causes of the Upper Points A_3 and A_2 in Carbonless Iron. — It has been seen that at these points spontaneous evolutions or absorptions of heat occur in chemically pure iron which, since they are not accompanied by any change of state (the metal being considerably below its solidification point) must, it seems, necessarily indicate the existence of iron under three allotropic forms. It has been mentioned in Lesson II that the allotropic form stable above A_3 is known as γ (gamma) iron, that stable between A_3 and A_2 as β (beta) iron, and the form stable below A_2 as α (alpha) iron. The following then takes place during the cooling and heating of pure iron: as the metal cools from a high temperature when the point Ar_3 is reached, it passes from the gamma to the beta condition with evolution of heat, while at Ar_2 it passes from the beta to the alpha form also with evolution of heat. On heating the reversals take place, the iron passing with absorptions of heat from the alpha to the beta condition at Ac_2 and from the beta to the gamma condition at Ac_3. That the point A_3 indicates an allotropic transformation is universally admitted, no one doubting the

existence of iron in at least two allotropic conditions. Most authoritative believe with Osmond that the point A_2 also indicates an allotropic transfor and that iron, therefore, assumes three distinct allotropic forms, as explained

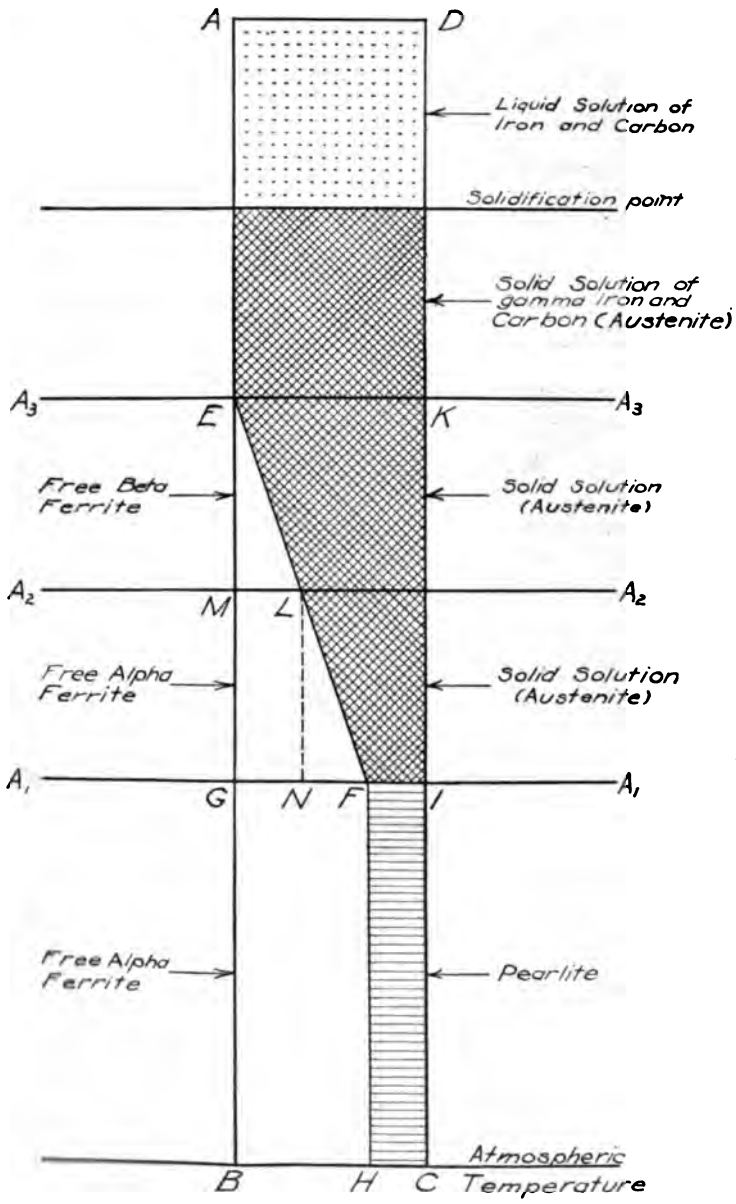

Fig. 1. Diagram depicting structural changes in 0.20 per cent carbon steel as it cools slowly from the molten condition to atmospheric temperature.

As eminent an observer as Le Chatelier, however, has expressed doubts as allotropic character of the point A_2. His reasons will be considered later. I lessons from will be assumed to exist in three allotropic conditions, of which

A_2 are the transformation points, this being the generally accepted theory and, in the author's opinion, the most probable one.

Causes of the Upper Critical Points A_3 and A_2 in Low Carbon Steel. — As might be expected the points A_3 and A_2 occurring in very low carbon steel also indicate allotropic changes in the metal. According to most writers, however, only that portion of the metal which at ordinary temperature exists as free ferrite is here affected. To make this matter clear it will be necessary to anticipate somewhat our subject, while the diagram shown in Figure 1 will be useful.

In this diagram the three critical points of steel containing 0.20 per cent carbon, A_3, A_2, and A_1, as well as its solidification point and atmospheric temperature are represented by parallel lines drawn at suitable intervals in the scale of temperature. The metal is represented by the rectangular area *ABCD*. The diagram illustrates the following facts later to be discussed at greater length: (1) in the molten condition steel is considered to be a liquid solution of iron and carbon, (2) on reaching its solidification point the metal is converted into a solid solution of gamma iron and carbon known as austenite, (3) upon reaching Ar_3 some ferrite begins to be set free, (4) the ferrite as it is set free assumes the beta state, this liberation of ferrite and its allotropic transformation being probably one and the same phenomenon, (5) the formation of free ferrite continues as the steel cools from Ar_3 to Ar_1, *EFG* representing the ferrite thus liberated, (6) on reaching the point Ar_2 the ferrite liberated between Ar_3 and Ar_2, *ML* in the diagram, passes from the beta to the alpha condition, (7) the ferrite liberated between Ar_2 and Ar_1, *LNF* in the diagram, assumes the alpha condition (according to some writers) without passing by the beta condition, while in the opinion of others the beta condition is assumed but is immediately followed by the alpha state, (8) while ferrite is being set free, the balance of the steel, *EKIF*, (according to most writers) preserves its condition of solid solution, gamma iron plus carbon, (9) upon reaching the point Ar_1 the residual solid solution, FI_1, is converted bodily into pearlite, (10) from Ar_1 down to atmospheric temperature no further structural change takes place, the steel being finally made up of $BH = GF$ per cent ferrite and of $HC = FI$ per cent pearlite.

On heating the opposite changes take place: (1) at Ac_1 transformation of FI pearlite into FI solid solution (gamma iron + carbon = austenite), while this solid solution begins immediately to assimilate some of the free ferrite, which as it is assimilated passes to the gamma condition, (2) between A_1 and A_3 absorption of free ferrite continues, being completed at Ac_3, (3) on reaching the point Ac_2 the ferrite, *ML* in the diagram, which has not been absorbed between Ac_1 and Ac_2 now passes to the beta condition. This diagram depicts accurately the generally accepted views in regard to the meaning of the critical points. If these views are correct several interesting inferences may be drawn as to the relative intensities of the critical points. The point A_3 in low carbon steel does not indicate a complete transformation, as too often loosely stated, but merely the *beginning*, at Ar_3, or the *end*, at Ac_3, of a transformation extending over a considerable range of temperature, i.e. from A_1 to A_3. Theoretically, therefore, it would seem as if the point A_3 must correspond to a mere change of direction in cooling and heating curves rather than to well-marked jogs. The fact that a decided jog marks the point Ar_3 in very low carbon steel might be ascribed to hysteresis, the metal cooling to a temperature below that at which the A_3 change is due so that when the transformation begins to take place it does so with added intensity, hence the jog. The jog corresponding to the Ac_3 point of very low

carbon steel is not so readily explained. But is not this jog much less pronounced than the one corresponding to Ar_3? The point Ar_2 marks (1) a complete transformation, namely, the passage from the beta to the alpha state of the free ferrite liberated between Ar_3 and Ar_2 and (2) the beginning of a transformation, namely, the passage to the alpha condition of the ferrite which continues to be liberated between Ar_2 and Ar_1. Because of the complete transformation implied by the point A_2 we readily understand that it should correspond to a jog both in the heating and cooling curves, and since Ar_2 is due chiefly to the allotropic transformation of the ferrite liberated between Ar_3 and Ar_2, we readily understand why it should occur at nearly the same temperature regardless of the carbon content. In the light of what precedes, however, the point A_3 in steel instead of being regarded as the manifestation of transformations occurring and completing themselves at a certain temperature, in reality indicates the *beginning* or *end* of transformations extending over considerable range of temperature, namely, from A_3 to A_1.

Cause of the Point $A_{3.2}$. — It has been seen that the point $A_{3.2}$ is apparently a merging of the points A_3 and A_2 of lower carbon steel and it seems natural to infer that the transformations which these points indicate, namely, the two allotropic changes, are here likewise merged, that is, that they now take place at the same temperature. In other words that when the point $Ar_{3.2}$ is reached on cooling the iron passes from the gamma to the beta and then immediately to the alpha state, the heat evolved being due to this double allotropic transformation. Some writers have claimed, however, that at the point $Ar_{3.2}$ the iron passes directly from the gamma to the alpha condition, the change of gamma to beta being suppressed in steel containing over 0.35 per cent carbon or thereabout. If such hypothesis were true it would have some important bearing upon the probable theory of the hardening of steel as explained in another lesson. In the author's opinion the more generally accepted view is better supported by experimental facts and other evidences and in these lessons the point $A_{3.2}$ will be considered as implying a double allotropic change. Most metallographists believe that like the independent points A_3 and A_2 the double point $A_{3.2}$ is the result of allotropic changes affecting the free ferrite only.

This setting free and allotropic transformation of ferrite is depicted diagrammatically in Figure 2 in the case of steel containing 0.60 per cent carbon and having, therefore, the two critical points $A_{3.2}$ and A_1. *EGF* indicates the gradual liberation of ferrite and its conversion to the alpha state as the metal cools from $Ar_{3.2}$ to Ar_1, the steel, after complete cooling, being made up of $BH = GF$ per cent ferrite and $CH = FI$ per cent pearlite.

If, as generally stated, the allotropic transformation of which $A_{3.2}$ is a manifestation affects only the free (pro-eutectoid) ferrite, the intensity of the point $A_{3.2}$ must decrease rapidly with decreasing pro-eutectoid ferrite, i.e. as the eutectoid composition is approached, and this point must vanish altogether as it meets the point A_1 (see Lesson VII, Fig. 2), from which it further follows that the single point of eutectoid steel is not in reality a triple point as the notation $A_{3.2.1}$ would imply, resulting from the merging of A_1 and $A_{3.2}$, but that on the contrary it remains a single point, being merely the continuation of the A_1 point of hypo-eutectoid steel.

Cause of the Point A_1. It has been seen that the point A_1 does not occur in carbonless iron, only feebly in iron containing little carbon, and with increased intensity as the carbon increases to the eutectoid point. The conclusion seems irresistible that the point A_1 must be closely related to the carbon, that it must indicate

en change in its condition. If steel be rapidly cooled from above the point Ac_1 en treated with certain dilute acids, practically all the carbon escapes as hy- ons, whereas the same steel after slow cooling through Ar_1 when similarly

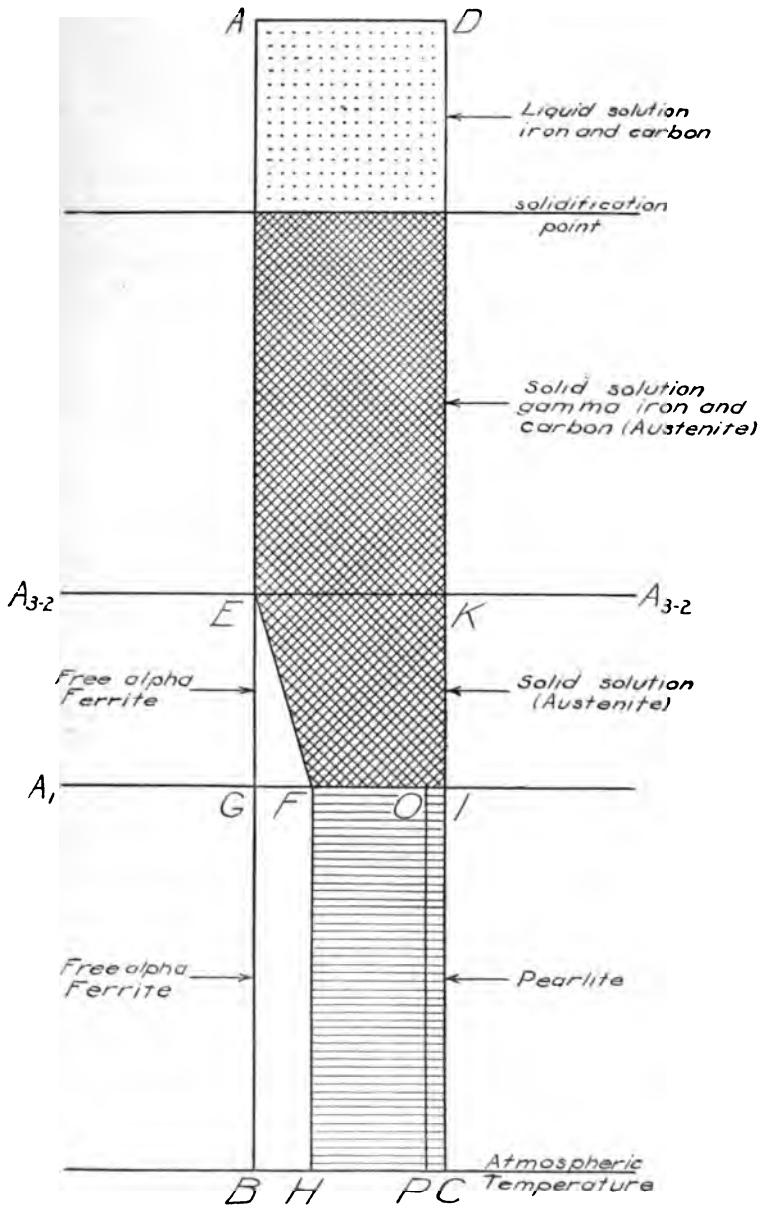

Fig. 2. — Diagram depicting structural changes in 0.60 per cent carbon steel as it cools slowly from the molten condition to atmospheric temperature.

yields a carbonaceous residue, which upon being analyzed is found to consist carbide Fe_3C. It is assumed that upon quick cooling we retain the carbon, ly at least, in the form in which it normally exists above A_1, and seeing that

when subjected to a similar treatment this carbon behaves so very differently from the carbon of slowly cooled steel, the conclusion is very logical that carbon exists above A_1 in a different condition from that normal below A_1. Above A_1 it is called "hardening" carbon, below A_1 "cement" carbon. On heating steel past the point Ac_1 the carbon changes from the cement to the hardening condition, and vice versa on cooling at Ar_1 from the hardening to the cement condition. It is, moreover, generally believed that this hardening carbon is carbon in solid solution in the iron. If it be so the heat evolved at Ar_1 is clearly in part at least the heat of formation of the carbide Fe_3C and the heat absorbed at Ac_1 clearly the heat of dissociation of that carbide which now is resolved again into its elements according to the reversible reaction

$$Fe_3C \rightleftarrows 3Fe + C.$$

The intensity of the A_1 point should then increase as the carbon increases or, rather, as the amount of pearlite increases, and should be maximum, therefore, at the eutectoid point as indicated in Figure 2, Lesson VII. With higher carbon content it diminishes slightly because the free (pro-eutectoid) cementite which is now present takes no part in the transformation occurring at Ar_1, having been formed at a higher temperature, namely, at Ar_{cm}, as later explained.

It would seem that the cause of the A_1 point, i.e. the point of recalescence, is in this way explained in a perfectly satisfactory manner. The correctness of this theory appears to be further supported by microscopical evidences which reveal the presence of Fe_3C in slowly cooled steel while pointing to the probable absence of it in suddenly cooled steel.

In recent years, however, it has seemed more and more probable to students of metallography that it is not carbon in its elementary state which is dissolved in iron at a high temperature, but rather the carbide Fe_3C itself and that the difference between the behavior of the carbon in hardened steel and in slowly cooled steel might well be satisfactorily accounted for on the ground that in hardened steel Fe_3C is *dissolved* in iron and in that form is much more readily acted upon by acids, being thereby converted into hydrocarbons, whereas Fe_3C when in the free crystallized condition, as in slowly cooled steel, resists the action of the acids and remains undissolved. If it is Fe_3C and not C which is dissolved in iron above the critical range, it is evident that the point Ar_1 cannot be caused by the *formation* of Fe_3C. But it may well be due to the crystallization or falling out of solution of Fe_3C. To be sure this is a falling out of a solid solution, but cannot we conceive that the falling out of a constituent of a solid solution is accompanied by an evolution of heat even if it does not imply a change of state? In other words is it not possible, or even probable, that crystallization in the solid state is accompanied by an evolution of heat? Surely this crystallization implies an allotropic or at least a polymorphic transformation and are not such transformations always accompanied by heat evolutions?

The author offers these thoughts as possibly worthy of attention and as a possible explanation of the evolution of heat at Ar_1 if we assume that Fe_3C and not C, as it now seems so probable, is dissolved in iron above that point.

The Point A_1 an Allotropic Point. — Most writers describe the point A_1 as purely a carbon point, that is, a manifestation of a change affecting the condition of the carbon only as explained in the foregoing pages. These same writers, however, assert that the upper critical points, A_3 and A_2 in low carbon steel or $A_{3,2}$ in higher carbon steel, affect only the condition of the free (pro-eutectoid) ferrite. In this they

are inconsistent, for if the upper point or points indicate allotropic transformation of the free ferrite only then the lower point A_1 is decidedly an allotropic point seeing that it corresponds to allotropic transformations of the pearlite-ferrite and that in steel containing more than some 0.40 per cent carbon there is more pearlite-ferrite than free ferrite. In other words the point A_1 is always an allotropic point indicating an allotropic transformation of the pearlite-ferrite similar to the allotropic transformation of the free ferrite occurring at the upper points, and in case of steel with more than 0.40 per cent carbon the allotropic change taking place at A_1 affects a larger bulk of iron than the change at $A_{3.2}$. To make the matter clear let us consider (Fig. 2) a steel containing some 0.60 per cent of carbon and, therefore, made up after slow cooling of 72 per cent of pearlite and 28 per cent of free ferrite. This steel will contain about $72 \times \frac{7}{8} = 63$ per cent of pearlite-ferrite represented by *FO* in Figure 2. When the point A_1 is reached this 63 per cent of iron is still in the gamma condition (according to the general belief) and now passes to the alpha condition either directly or first assuming the beta state. The allotropic character of the point A_1 is therefore evident. Indeed it is sufficient to account for the heat evolved at Ar_1 or absorbed at Ac_1 without the assistance of any change occurring in the carbon condition, for it is in perfect agreement with the increased intensity of the point A_1 as the carbon increases and with its maximum at the eutectoid composition, since as the carbon increases the amount of pearlite and therefore of pearlite-ferrite likewise increases.

Summing up, three reasons may be given for the evolution of heat at Ar_1: (1) formation of the carbide Fe_3C based on the assumption that carbon as such is dissolved in iron, (2) crystallization of the carbide Fe_3C based on the assumption that this carbide is dissolved in iron and that crystallization not implying a change of state may produce heat, and (3) allotropic transformation of the iron present in austenite of eutectoid composition. It seems probable that both (2) and (3) contribute to the heat developed at Ar_1.

Pearlite Formation. — Whatever differences of opinion may exist as to the exact cause or causes of the evolution of heat corresponding to the point Ar_1 all agree that it is due to the transformation of austenite of eutectoid composition (sometimes called hardenite) into pearlite, i.e. the conversion of a solid solution into an aggregate (ferrite plus cementite). It is well to bear in mind the changes in the condition of the iron and carbon which this transformation seems to imply: (1) passage of the iron from the gamma to the beta condition, (2) immediately followed by its conversion into alpha iron or, according to some writers, (1 and 2) the conversion of gamma iron directly into alpha iron, skipping the beta state, (3) the crystallizing of alpha iron into parallel plates or lamellæ, and (4*a*) the formation and crystallizing or (4*b*) the crystallizing only of Fe_3C into parallel plates alternating with the ferrite plates.

Cause of the Point A_{cm}. — The point Ar_{cm} undoubtedly indicates the beginning of the liberation of free cementite in hyper-eutectoid steel as it cools from Ar_{cm} to $Ar_{3.2.1}$. This gradual formation of free cementite is well shown in Figure 3 where it is represented by the triangle *EFG*. When the point $A_{3.2.1}$ is reached the residual austenite, now of eutectoid composition, is converted bodily into pearlite, the steel consisting finally of $BH = GF$ per cent free cementite and $DC = FI$ per cent pearlite. It will be seen that this upper point of hyper-eutectoid steel, like the points A_3 and A_2 of hypo-eutectoid steel, does not indicate a complete transformation but

merely the beginning of a transformation covering a wide range of temper namely, from A_{cm} to $A_{3.2.1}$. If it corresponds to a jog rather than to a mere c of direction in cooling curves this must be ascribed to hysteresis and its tende

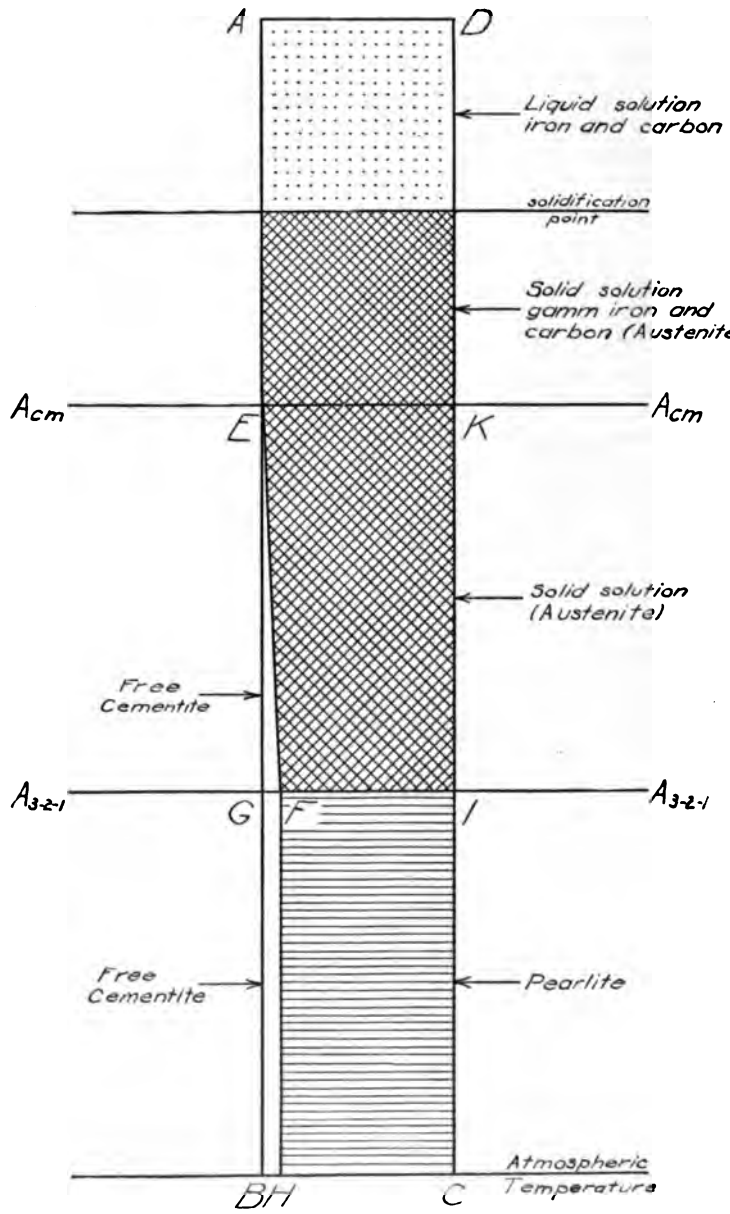

Fig. 3. — Diagram depicting structural changes in 1.25 per cent carbon steel as it cools slowly from the molten condition to atmospheric temperature.

accentuate the beginning of a transformation as previously explained. The tion of heat corresponding to the liberation of free cementite may be explai two ways: (1) actual formation of Fe_3C, carbon and not the carbide being in so

above Ar_{cm}, or (2) crystallization or falling out of solution of Fe_3C based on the more probable assumption that Fe_3C and not C is dissolved by the iron above Ar_{cm}, and on the further assumption that this crystallization in the solid state, since it evidently implies an allotropic or, at least, polymorphic change, must be accompanied by an evolution of heat.

Since in hyper-eutectoid steel containing even as much as 1.5 per cent carbon there is but a small proportion of free cementite (some 11 per cent) the point Ar_{cm} is caused by the evolution of but a small amount of heat and must therefore be faint. Its intensity, moreover, must decrease as the carbon decreases and the point must disappear altogether as the eutectoid composition is reached, that is, just as it meets the single point of eutectoid steel. This is indicated in Figure 2 of Lesson VII.

Allotropy of Cementite. — If we believe, as most metallographists now do, that Fe_3C and not C forms a solid solution with carbon above the point A_1 or $A_{3.2.1}$, it follows that this dissolved Fe_3C crystallizes or falls out of solution at certain critical temperatures, namely, Ar_{cm} for the free cementite of hyper-eutectoid steel and Ar_1 (or $Ar_{3.2.1}$) for the pearlite-cementite of all steels, and that this crystallization is accompanied by an evolution of heat. This falling out of solution really implies a spontaneous change of crystalline form and is therefore an evidence of polymorphism, hence of allotropy, for if allotropy does not necessarily imply polymorphism, polymorphism implies allotropy. Are we not then justified in believing that Fe_3C may exist under two allotropic forms: (1) an allotropic variety soluble in iron, which we may call gamma cementite and (2) an allotropic variety insoluble in iron, which we may call alpha cementite, constituting the free cementite of hyper-eutectoid steel and the hard plates of pearlite?

The fact that the crystallizing or falling out of solution of free ferrite in hypo-eutectoid steel implies an allotropic transformation of the liberated ferrite, points with force to a similar transformation forming part of the liberation of free cementite in hyper-eutectoid steel. In the case of iron we are able to actually prove this allotropy through the cooling of very pure iron and the testing of its properties while in the case of cementite such direct proof is not yet at hand because of the difficulty of obtaining pure cementite and of testing it after producing it.

To generalize, it would seem as if the crystallizing or falling out of solution of a substance at certain critical temperatures always implies a spontaneous change of crystalline form and, therefore, an allotropic transformation of the substance separating from the solution, whether that solution be liquid or solid. In the former case the falling out of solution implies a change of state, the separating substance passing from the liquid to the solid state, but does it make it less of an allotropic change? Allotropic transformations which also imply changes of state might be called instances of major allotropy to distinguish them from those instances in which changes of internal energy are not accompanied by changes of state.

Cause of the Point $A_{3.2.1}$ in Eutectoid Steel. — In the case of eutectoid steel the solid solution (austenite) is originally of eutectoid composition and, therefore, on cooling reaches the point $Ar_{3.2.1}$ without rejecting either ferrite or cementite, hence the absence of upper points in eutectoid steel. On passing through the point $Ar_{3.2.1}$ (Fig. 4) this austenite is converted into pearlite. Pearlite contains 87.50 per cent of ferrite which undergoes allotropic transformation at $Ar_{3.2.1}$, hence the intense allotropic character of this point. The crystallizing of cementite probably contributes also to the heat evolved at $Ar_{3.2.1}$ whether it implies the *formation* of Fe_3C or

not as explained before. It has also been argued that this crystallizing of ce probably implies an allotropic transformation, in which case the point $A_{3.2.1}$

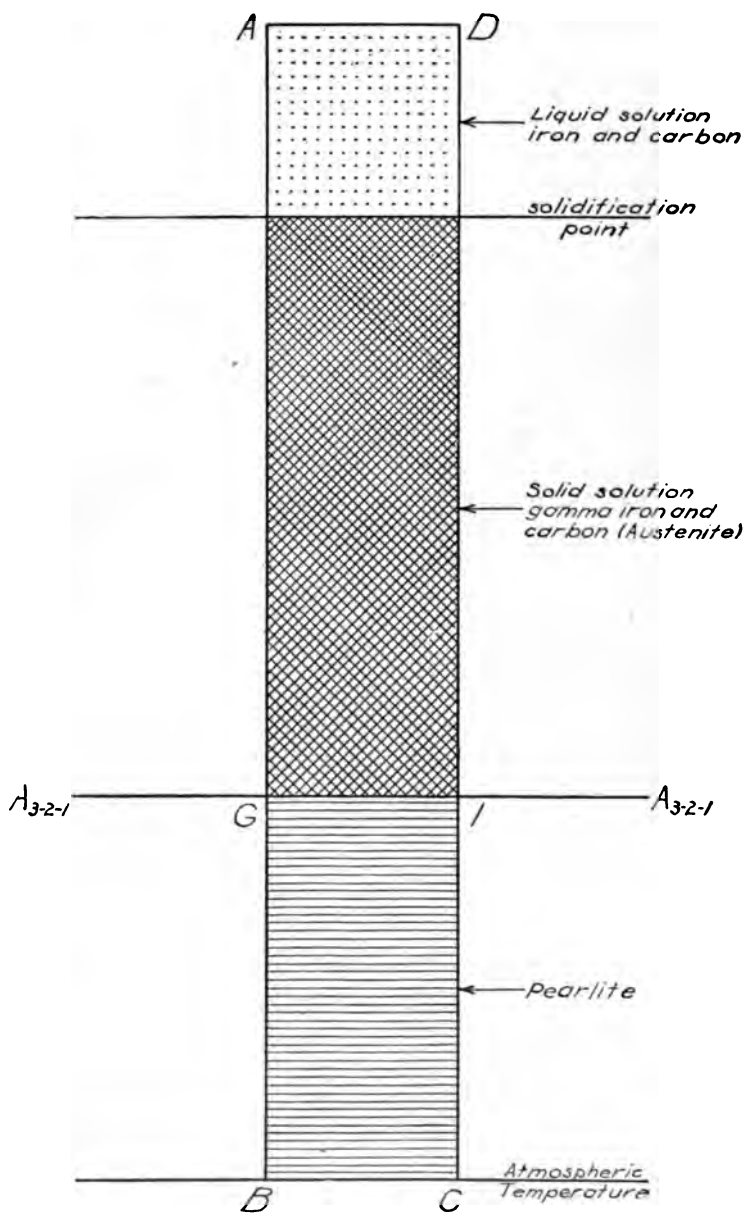

Fig. 4. — Diagram depicting structural changes in eutectoid steel as it cools slowly from the molten condition to atmospheric temperature.

as well) would be solely an allotropic point, resulting from the simultaneou tropic transformation of both the iron and the Fe_3C of austenite of eu composition.

Finally let us bear in mind that notwithstanding its notation the single p

eutectoid steel does not in fact result from the merging of the several points of hypo-eutectoid steel, being merely a continuation of the point A_1. This point A_1 is essentially a "pearlite" point while the upper points of hypo-eutectoid steel are "ferrite" points and the upper point of hyper-eutectoid steel is a "cementite" point.

Cause of the Point $A_{3.2.1}$ in Hyper-Eutectoid Steel. — The point $A_{3.2.1}$ in hyper-eutectoid steel is of exactly the same nature as the point $A_{3.2.1}$ of eutectoid steel and the point A_1 of hypo-eutectoid steel. It marks the formation of pearlite, bearing in mind the various changes in the condition of the carbon and iron implied by that formation. As the proportion of pearlite now decreases with increase of carbon the intensity of the point $A_{3.2.1}$ likewise diminishes.

Formation of Beta Iron. — Allusion has been made in these pages on several occasions to the different opinions entertained as to the formation of beta iron in steel of various carbon contents. The matter should receive additional attention. The following views are held: (1) iron in carbonless iron and in all grades of steel passes from the gamma to the beta condition before assuming the alpha state, the absence of an independent A_2 point in medium high and in high carbon steel notwithstanding, (2) iron passes from the gamma to the beta condition only in those grades of iron and steel which exhibit the point A_2, and, therefore, only in carbonless iron and in steel containing less than some 0.30 per cent carbon, in higher carbon steel the iron passing directly from the gamma to the alpha state, (3) the beta condition does not exist even in carbonless iron, the point A_2 not being an allotropic point.

Of these three different views the first is the one most generally accepted and, in the author's opinion, best supported by evidence. It will be seen in another lesson to afford the most acceptable theory of the hardening of steel. The second view is based entirely upon the absence of the A_2 point in steel containing more than 0.30 per cent carbon, a very weak foundation, for there is no reason why the points $A_{3.2}$ and $A_{3.2.1}$ cannot include the gamma-to-beta transformation. The third view advanced by Le Chatelier will require more convincing arguments in order to uproot the belief that the point A_2, occurring as it does in the purest iron and, as will be shown later, marking a sudden and pronounced change in its magnetic properties, is an allotropic point.

Summary. — The apparent causes of the thermal critical points of iron and steel may be briefly summed up as follows:

The point Ar_3 of carbonless iron and of steel containing less than some 0.35 per cent carbon marks the beginning of the liberation of ferrite (which liberation continues down to the point Ar_1) and the transformation of that ferrite from the gamma to the beta condition, this setting free of ferrite and its allotropic transformation being probably simultaneous.

The point Ar_2 of carbonless iron and of steel containing less than some 0.35 per cent carbon indicates the transformation from the beta to the alpha condition of the ferrite liberated between Ar_3 and Ar_2 and the beginning of the passage of the ferrite, which continues to be liberated as the metal comes from Ar_2 to Ar_1, from the gamma to the beta and then to the alpha condition or, as some writers claim, directly from the gamma to the alpha state.

The point $Ar_{3.2}$ of steel containing somewhere between 0.35 and 0.85 per cent carbon marks the beginning of the liberation of ferrite which takes place between $Ar_{3.2}$ and Ar_1 and the passage of that ferrite from the gamma to the beta condition

and immediately to the alpha state or, according to some writers, directly from the gamma to the alpha condition.

Since only the formation and transformation of free ferrite is involved at the points A_3, A_2, and $A_{3.2}$ these points may properly be called "ferrite" points.

The point A_1 of hypo-eutectoid steel, as well as the point $A_{3.2.1}$ of eutectoid and hyper-eutectoid steel, marks the rather sudden transformation of the residual solid solution (austenite), now of eutectoid composition, into pearlite, bearing in mind the changes in the conditions of the iron and carbon which such transformation implies. The points A_1 and $A_{3.2.1}$ may properly be called "pearlite" points.

The point Ar_{cm} of hyper-eutectoid steel marks the beginning of the setting free of cementite as the metal cools from Ar_{cm} to $Ar_{3.2.1}$, the liberation of cementite probably involving an allotropic change of that constituent as previously explained.

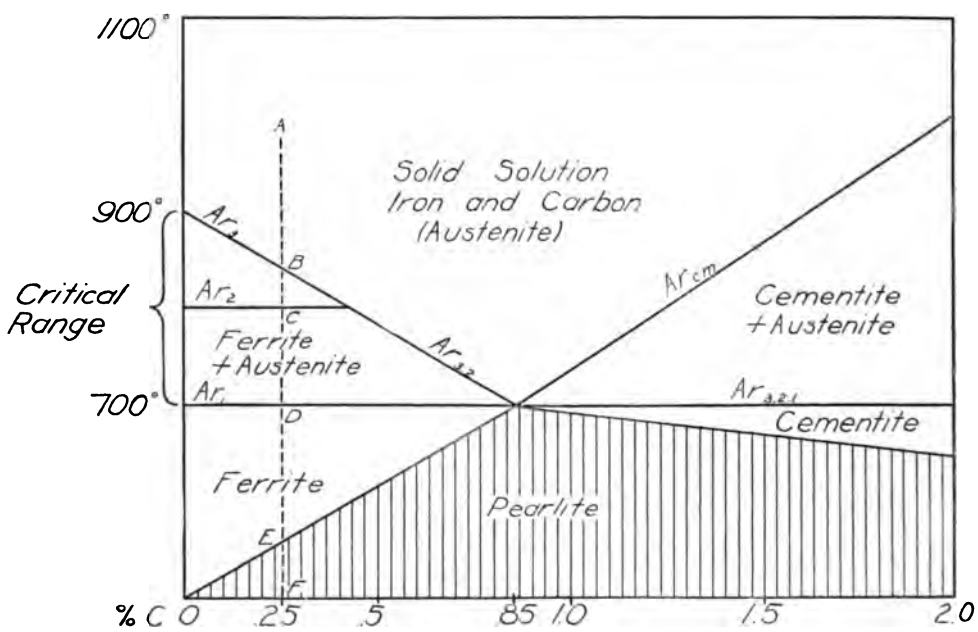

Fig. 5. — Diagram showing the relation between the critical points and the structural composition of slowly cooled steel.

In Figure 5 an attempt has been made at showing diagrammatically the relation between the critical points of steel and its structural composition after slow cooling. It will be readily understood. The upper part of the diagram shows the location of the critical points, the lower part the structural composition in percentages of ferrite, pearlite, and cementite. Taking, for instance, a steel containing 0.25 per cent carbon: above A_3 at *A* it is a solid solution of carbon and iron (austenite); on cooling through Ar_3 at *B* some beta ferrite is set free, this liberation continuing from *B* to *C;* on cooling through Ar_2 at *C* the free beta ferrite is converted into alpha ferrite while additional alpha ferrite forms as the metal cools to Ar_1, that is from *C* to *D*. The ferrite liberated on cooling from *B* to *D*, that is on cooling through the critical range, is represented in the lower part of the diagram by *DE* which is also the final percentage of free ferrite in the steel. As the metal cools through its Ar_1 point at *D*, the residual

austenite, at present of eutectoid composition, is converted into pearlite, *EF* representing the pearlite here formed, i.e. the percentage of pearlite in the steel. The

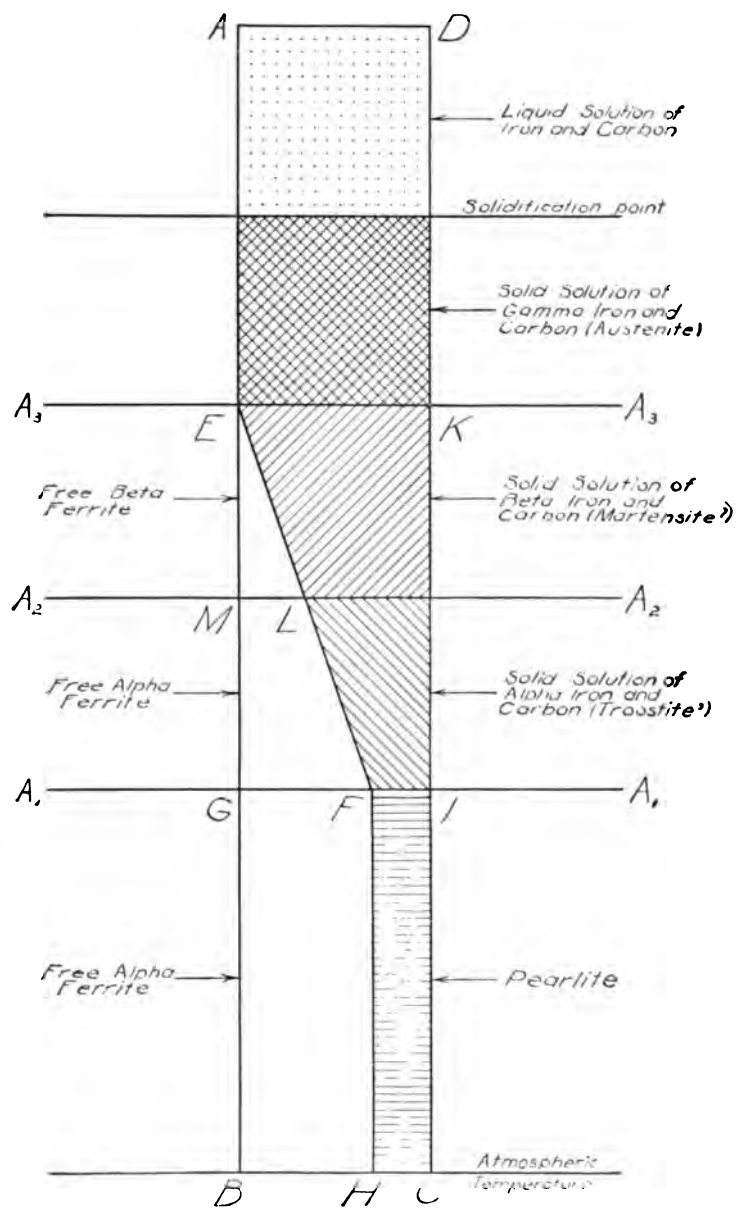

Fig. 6. — Diagram depicting structural changes in 0.20 per cent carbon steel slowly cooled, assuming that the iron remaining in solution as well as the free iron (ferrite) undergoes allotropic changes. To be compared with Figure 1.

structural formation of any steel can be followed in the same way in this diagram. It will be obvious that the vertical distances representing the percentages of ferrite, pearlite, or cementite in any steel may also be regarded as proportional to the intensities

of the corresponding critical points. For instance, the distance *ED* may be assumed to be proportional to the combined intensities of the points Ar_3 and Ar_2 of a 0.25 per cent carbon steel and the distance *EF* proportional to the intensity of the A_1 point. Interpreted in this way the diagram indicates what has already been pointed out: (1) that the intensities of A_3 and A_2 decrease as the carbon increases, these points vanishing on reaching the eutectoid composition, (2) that the point A_1, very faint at first, increases rapidly with increased carbon, becoming maximum at the eutectoid point and then decreasing, and (3) that the point A_{cm}, always faint, increases slightly as the carbon increases above 0.85 per cent.

Another View of the Allotropic Changes. — It will be obvious from the description of the underlying causes of the critical points given in the foregoing pages that, according to the general belief, iron must first be freed from solid solution before it can undergo any allotropic changes or, at least, its liberation from solution and its allotropic transformation take place simultaneously, the latter never preceding the former. In 1906 the author expressed the opinion that it was far from certain that its liberation from solution must precede, or at least be simultaneous with, the allotropic changes affecting iron at certain critical temperatures. He ventured to put forward, in a tentative way, the hypothesis that iron in solution might first undergo an allotropic transformation and then be expelled in its new allotropic form. This view was not favorably received but, as it has not been shown to be by any means untenable, the author still believes it worthy of record in these pages. It is evident that if the allotropic transformation of iron from the gamma to the beta and then to the alpha state precedes its liberation from solution, three solid solutions of carbon in iron are formed during the slow cooling of steel, namely, carbon (or the carbide Fe_3C) dissolved (1) in gamma iron, (2) in beta iron, and (3) in alpha iron. The first solid solution is universally called austenite while the hypothesis leads almost irresistibly to regarding the solid solution in beta iron as martensite and the solid solution in alpha iron as troostite, two constituents to be described in another lesson.

With the assistance of the diagram, Figure 6, and by comparing it with Figure 1 the working of the present hypothesis will be readily understood. In Figure 6 are depicted the structural changes taking place during the slow cooling of steel containing 0.20 per cent carbon and therefore exhibiting the three critical points A_3, A_2, and A_1. On cooling through the point A_3 the solid solution of carbon and gamma iron (austenite) existing above A_3 is converted into a solid solution of carbon in beta iron (martensite?). In the beta condition, however, iron cannot be retained in solution and begins immediately to be liberated, and its liberation continues as the metal cools down to A_2. Between A_3 and A_2 we have a solid solution of beta iron decreasing in amount and increasing free beta ferrite. On cooling through Ar_2 both the free beta ferrite and the dissolved beta ferrite pass to the alpha state, giving rise to the formation of free alpha ferrite and of a solution of carbon in alpha iron (troostite?). On cooling from Ar_2 to Ar_1 additional alpha ferrite is liberated while the proportion of carbon-alpha iron solution decreases correspondingly. At Ar_1 the remaining solution has become of eutectoid composition and is converted bodily into pearlite, the mechanism of this transformation being well understood. It will be evident that in the case of hypo-eutectoid steel having but one upper critical point, $Ar_{3.2}$, in cooling through that point the metal would pass from the condition of a solid solution of carbon in gamma iron to that of a solid solution in beta iron and then immediately to that of a solid solution in alpha iron, the steel between $Ar_{3.2}$ and Ar_1 being composed of this solution in alpha iron (troostite?) and of free alpha ferrite. With eutectoid steel the following changes would take place as it cools through its single critical point $Ar_{3.2.1}$: (1) transformation of gamma iron solid solution (austenite) into beta iron solid solution (martensite?); (2) immediately followed by the formation of alpha iron solid solution (troostite?); (3) immediately followed by formation of pearlite.

The author thinks that the decreasing intensities of the points A_3 and A_2 as the carbon content increases is the fact most difficult to reconcile with the hypothesis just outlined, for if these points are due to allotropic transformations affecting the entire bulk of the steel their intensities should be quite independent of the amount of carbon present. To be sure, this gradual diminution of the magnitude of the points A_3 and A_2 as the carbon increases is likewise difficult of explanation in the light of the universally accepted hypothesis that free iron only can be allotropically transformed, for it has been made clear in the foregoing pages that these points must indicate then the *beginnings of* transformations and not transformations carried to completion at those critical points, so that the

*in*tensities of the points should be little affected by the magnitude of the transformations themselves, that is, by the amount of free ferrite undergoing allotropic transformation or, which is the same thing, by the percentage of carbon in the steel.

The view just outlined as to the mechanisms of the allotropic changes is further depicted dia-

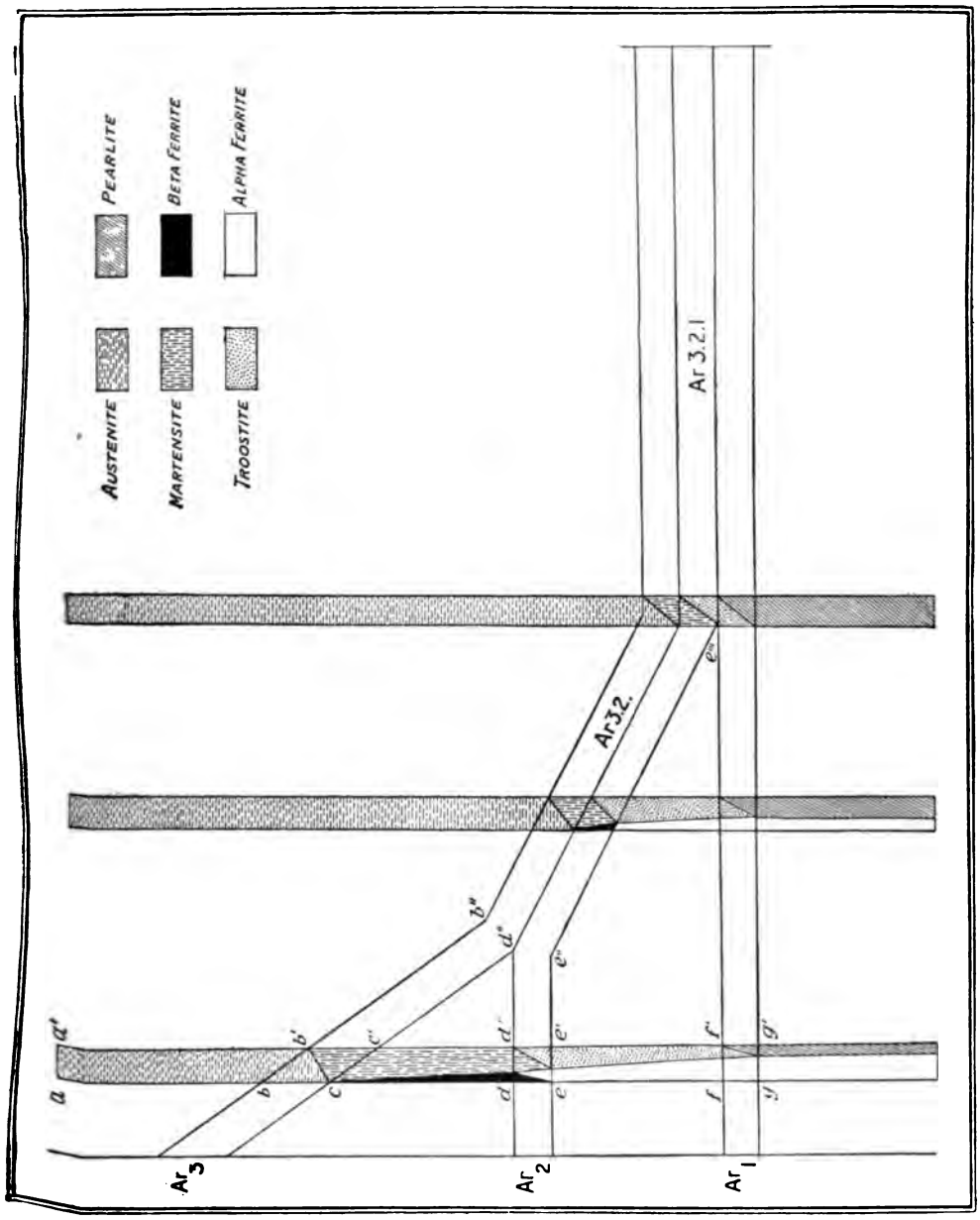

Fig. 7

grammatically in Figure 7, in which the critical points are represented as covering certain ranges of temperature making it possible to show, graphically, the changes taking place within these ranges. Taking an iron carbon alloy having, for instance, the composition *a* (some 0.20 per cent carbon), the diagram shows that above Ar_3 it is made up of *aa'*, i.e. of 100 per cent austenite; on cooling through Ar_3 it is gradually converted into martensite; between Ar_3 and Ar_2 beta ferrite is

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LESSON IX

THE THERMAL CRITICAL POINTS OF IRON AND STEEL

THEIR EFFECTS

It has been shown in preceding lessons that the thermal critical points of iron d steel are due chiefly if not wholly to allotropic transformations of the iron. It is vell-known fact that when a substance undergoes an allotropic transformation ny of its properties undergo likewise deep and sudden changes at the critical peratures. Color, crystallization, dilatation, conductivity both for heat and elec- ity, strength, ductility, hardness, specific gravity are properties frequently affected , body passes from one allotropic form to another. We should expect, therefore, ı changes to take place, as iron undergoes its allotropic transformations, if not in at least in some of the above properties. And it is because such changes do take e that a clear understanding of the occurrence and significance of the critical ts is of much practical importance to the iron and steel metallurgist.

Changes at A_3

t has been shown that the point A_3 occurs in carbonless iron and in steel con- ing less than some 0.35 per cent of carbon and that it is universally believed that point indicates an allotropic change, the iron passing from the gamma to the condition on cooling at Ar_3, and vice versa, from the beta to the gamma condi- on heating at Ac_3. It should be borne in mind, however, as fully explained in on VIII that the general belief is that free ferrite only undergoes this change. he metal cools past its point Ar_3 the following abrupt changes in some of its erties have been noted.

Dilatation. — The metal, which above the point Ar_3 was contracting, as is the ral rule with all cooling bodies, on passing through the point Ar_3 undergoes sud- y a marked dilatation, amounting to over $\frac{1}{100}$ of its length, immediately fol- d again by a normal contraction. Such dilatation implies that the change of ma into beta iron takes place with augmentation of volume, or in other words gamma iron is denser, has a higher specific gravity than beta iron. The dilata- s occurring at Ar_3 in the case of steels containing respectively 0.05 and 0.15 per carbon are shown graphically in Figure 1. On heating, at Ac_3 a spontaneous raction occurs of the same magnitude as the dilatation on cooling. Had we no r evidence of an allotropic transformation of the iron at this critical tempera- this sudden dilatation taking place as it does in pure iron would justify our f in its existence.

lectrical Conductivity. — Above the point A_3 the metal has an electrical resis- e some ten times greater than its resistance at ordinary temperature. As it cools a high temperature to the point Ar_3 there is but a feeble decrease of its electrical

resistance, but as soon as Ar_3 is reached it begins abruptly and sharply to decrease and keeps on decreasing at a normal rate to atmospheric temperature. At A_3, therefore, we have a sudden and marked change in the variation of the electrical conductivity corresponding to a sharp break in the curve expressing the relation between temperature and electrical resistance as shown in Figure 2. On heating, at Ac_3 the opposite change takes place, that is, the electrical resistance quite suddenly ceases to increase. So marked and sudden a change in a physical property is in itself a proof of an allotropic transformation.

Crystallization. — It has been shown in Lesson II that while gamma and beta iron both crystallize in the cubic system (Osmond) octahedra are the prevailing form of gamma iron while the cube is the crystalline form of beta iron, and that the trans-

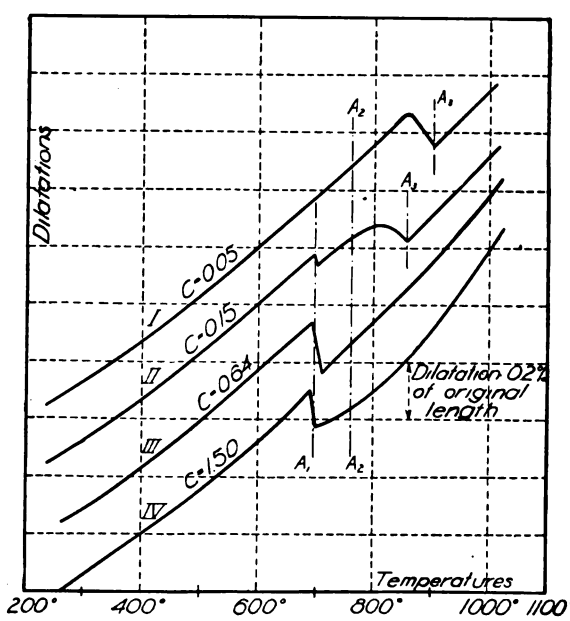

Fig. 1. — Dilatation curves of various carbon steels.

formation of gamma into beta iron includes a change in the planes of symmetry, at least of carburized iron (Osmond). As already mentioned, however, the crystallographic differences between gamma and beta iron are not such as to prove the existence of these two allotropic varieties of iron.

Hardness, Ductility, Strength. — Evidences will be offered later to show that as the metal passes through the point Ar_3 the iron becomes harder, stronger, and less ductile; in other words that gamma iron is softer, more ductile, and weaker than beta iron.

Dissolving Power for Carbon. — Above the point A_3 iron possesses dissolving power for carbon, while according to some writers it loses that power on passing through Ar_3; in other words gamma iron can dissolve carbon but beta iron is deprived of that power. It does not, however, seem, by any means, proven that beta iron cannot dissolve carbon, many authoritative workers holding the opposite view. The question will be discussed at greater length in another lesson.

Structural Properties. — It has been explained at length in Lesson VIII that the point Ar_3 corresponds to an abrupt structural change, namely, the beginning of the setting free of ferrite (Fig. 1, Lesson VIII).

Other Properties. — Le Chatelier mentions a change in the variation of the thermo-electric force and a sudden but slight variation in magnetic properties as taking place at A_3.

Changes at A_2

As a separate point A_2 occurs in carbonless iron and in steel containing less than some 0.35 per cent of carbon. The changes of properties taking place at A_2 are not generally as abrupt nor are they as marked as those occurring at the other critical points. It is precisely because of this lack of sharpness and suddenness that some metallographists, notably Le Chatelier, have questioned the accuracy of the generally accepted view that this point like A_3 indicates an allotropic transformation. Careful consideration of the evidences at hand appear to show, however, that changes

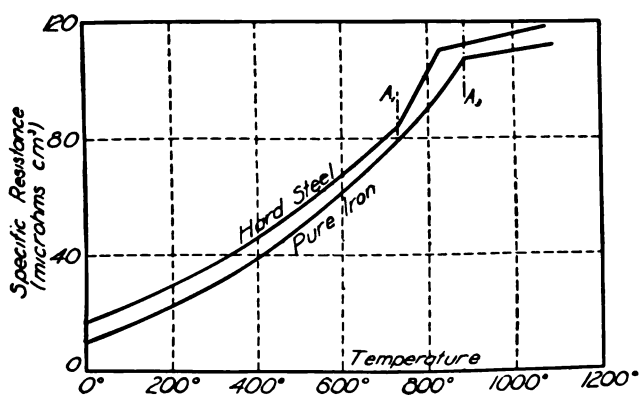

Fig. 2. — Electrical resistance curves of iron and high carbon steel.

of properties do occur at A_2 sufficiently marked and sudden to warrant the classification of this point as an allotropic one. The fact that these changes are more gradual than at the other critical points is logically explained by Osmond on the ground that beta and alpha iron are isomorphous, that is, capable of forming solid solutions and that therefore the passage of one variety into the other must necessarily be gradual as well as the variations of the properties of iron which the transformation implies.

Dilatation. — According to Le Chatelier, to Charpy and Grenet, and to some others, no dilatation takes place as the metal cools past the point Ar_2 and they see in this an indication that A_2 is not an allotropic point. Osmond's reply is that the curves obtained by Charpy and Grenet, for instance, do indicate a dilatation at Ar_2 which, however, the authors fail to notice because the transformation not being sudden the dilatation likewise is gradual, whereas the authors were looking for sudden dilatations only. If according to Osmond iron does expand on passing through the point Ar_2 the specific gravity of beta iron must be greater than that of alpha iron.

Magnetic Properties. — Above the point A_2 steel is non-magnetic, it is not attracted by a magnet, but in passing through Ar_2 it suddenly becomes strongly magnetic. Is not this abrupt and momentous change alone, in the magnetic properties of

...mation? It is true that ... temperature is reached ... fact remains that the *grea* ... acquired as it cools past the ... one can satisfactorily accoun ... of steel and the temperature ... and regains it on cooling is shown g ... diagram represent the average values ... Madame Sklodowska Curie with a seri ... that the points of magnetic changes ... A_1, A_2 or $A_{3.2.1}$. With little carbon th ... magnetism on cooling and its disappe ... A_2 occur at nearly the same tempera ... are lowered and so, likewise, the ... sistent with the greater gap between ... tic points are further lowered an ... being in harmony with the locati ... with the greater gap between $Ar_{3.2.1}$ a ... the points of magnetic transformat ... given in the following tables showi ... All the steels used in connection ... vicinity of one per cent carbon.

... THE MAGNETIC METHOD WITH TI ... CURVE METHOD. (BOYLSTON.)

			$Ar_{3\text{-}2\text{-}1}$		
	Max. Min.	Number of Tests	Mean	Max. Min.	
...	788 .759	7	708	.711 706	
794	781 754	4	718	.736 701	
	$Ar_{3\text{-}2}$			$Ar_{3\text{-}2}$	
789	.790 770	7	741	.750 734	
827	830 822	3	754	.756 753	
	Ac_2			Ar_2	
784	.772 .755	6	764	.771 758	
768	.772 764	2	767	.783 748	

TABLE II. — RESULTS OBTAINED BY STUDENTS AT HARVARD UNIVERSITY

Steel Number	Method	$Ac_{3\text{-}2\text{-}1}$	Number of Tests	$Ar_{3\text{-}2\text{-}1}$	Number of Tests
1	Magnetic	753	72	679	75
	Ordinary	739	14	688	12
2	Magnetic	752	131	695	136
	Ordinary	750	13	695	17
3	Magnetic	761	55	704	55
	Ordinary	757	55	708	55
4	Magnetic	762	50	700	50
	Ordinary	751	45	701	45
5	Magnetic	776	40	720	40
	Ordinary	760	30	727	30

Crystallization. — The cube being the crystalline form both of beta and of alpha iron and these two allotropic varieties being capable of dissolving each other in all

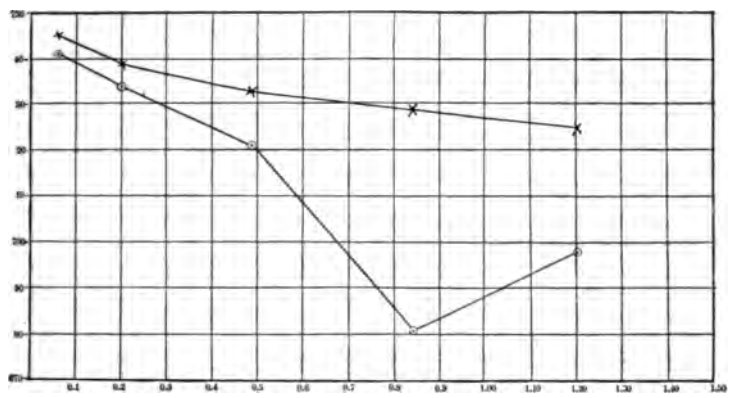

Fig. 3. — Temperatures of magnetic transformations of various carbon steels.

proportions (Osmond) a crystalline transformation at the point A_2 is not to be expected. The crystallography of iron so far as it has been investigated does not reveal the existence of the point A_2.

Hardness, Ductility, Strength. — It will be shown in another lesson that as the metal passes through the point Ar_2 it becomes softer, more ductile, and less tenacious, in other words that beta iron is harder, stronger, and less ductile than alpha iron.

Dissolving Power for Carbon. — Most metallographists believe that alpha iron does not possess any dissolving power for carbon, or at least that it is only capable of dissolving a very small amount of that element. On the other hand, as already mentioned, it is far from certain that beta iron is incapable of dissolving carbon, statements to the contrary notwithstanding. It is possible, therefore, that on cooling through Ar_2, iron loses its dissolving power for carbon.

Structural Properties. — By referring to Figure 1 of Lesson VIII it will be seen that there is no apparent structural change connected with the point A_2. As the steel cools past Ar_2 the liberation of ferrite started at Ar_3 merely continues, to end only at Ar_1. Of course the ferrite liberated above Ar_2 now passes from the beta to the alpha

condition but this allotropic transformation does not appear to include any structural change.

Other Properties. — Goerens and Cavalier both mention a sudden decrease in the specific heat of iron as taking place at Ac_2, and vice versa a sudden increase at Ar_2.

Changes at $A_{3.2}$

It has been shown that the point $A_{3.2}$ resulting from the merging of A_3 and A_2 occurs, theoretically at least, in steels containing from some 0.35 to 0.85 per cent carbon. As might be expected the changes of properties corresponding to the point $A_{3.2}$ are the same as those taking place in lower carbon steel at A_3 and A_2. As the metal cools through $Ar_{3.2}$ the following variations of properties are, therefore, noted: (1) a marked dilatation, (2) a sudden decrease of electrical resistance, (3) a gain of magnetism, (4) a probable loss of dissolving power for carbon, (5) the beginning of the liberation of alpha ferrite (see Lesson VIII, Fig. 2).

Changes at A_1

The point A_1 occurs in steel containing from a mere trace to 0.85 per cent carbon. It corresponds, as explained in Lesson VIII, to the transformation of the residual austenite (now of eutectoid composition) into pearlite. This formation of pearlite implies that the iron contained in this residual austenite (and forming about 85 per cent of its bulk) undergoes on cooling through Ar_1, the same allotropic changes as those affecting the free ferrite on cooling through Ar_3 and Ar_2 (or $Ar_{3.2}$). It follows from this that, theoretically at least, the following sudden changes of properties should be noted on cooling through Ar_1: (1) a dilatation increasing with the carbon content and being maximum with 0.85 per cent carbon caused by the allotropic transformation of the iron, (2) increased magnetism because of the transformation of additional non-magnetic gamma iron into magnetic alpha iron, (3) decreased electrical resistance because of additional transformation of high resistance gamma iron into low resistance alpha iron, and (4) additional loss of dissolving power for carbon because of the formation of additional alpha iron.

Of the above changes the dilatation only has been conclusively shown to occur and to increase with the carbon content (Fig. 1). The point A_1 has never, to the author's knowledge, been connected with critical variations of the electrical and magnetic properties of steel, but on purely theoretical ground he does not see how the conclusion can be avoided that such critical variations must exist provided of course that we are right in assuming that in austenite of eutectoid composition the iron is still in the gamma condition, that is, non-magnetic and of high electrical resistance. It is possible that if experiments were conducted with a view of detecting these variations, the results would confirm these theoretical deductions.

Changes at $A_{3.2.1}$

The point $A_{3.2.1}$ occurs in eutectoid and in hyper-eutectoid steel and marks the transformation of the austenite of eutectoid steel or of the residual austenite of hyper-eutectoid steel, into pearlite, as shown in Figures 3 and 4, Lesson VIII. In these steels, however, no liberation of free ferrite occurs above the point $Ar_{3.2.1}$ from which it follows that the *totality* of the iron undergoes its allotropic change or changes on passing through $Ar_{3.2.1}$. The variations of the properties which in hypo-eutectoid

teel occur at A_3, A_2, and A_1 must therefore, in the case of eutectoid and hyper-utectoid steel all take place at the point $A_{3.2.1}$. These sudden changes of properties re, on cooling: (1) a marked dilatation, maximum in eutectoid steel (Fig. 1), (2) a udden decrease of electrical resistance, (3) a sudden gain of magnetism, (4) a loss f dissolving power for carbon.

Le Chatelier mentions the fact that on cooling through Ar_1 or $Ar_{3.2.1}$ steel acquires a temporary malleability. If a steel bar, for instance, of sufficient length be held horizontally by one extremity while cooling, it at first remains rigid, but on passing through its point of recalescence it quite suddenly bends.

Changes at A_{cm}

The point Ar_{cm} occurs in hyper-eutectoid steel and marks the beginning of the liberation of free cementite as the metal cools from Ar_{cm} to $Ar_{3.2.1}$ (see Fig. 3, Lesson VIII). Except for this structural change no other marked changes of properties have so far been connected with this point.

Structural Change at A_1 and $A_{3.2.1}$. — The spontaneous transformation of austenite of eutectoid composition into pearlite, that is, of a solid solution into an aggregate, at Ar_1 or $Ar_{3.2.1}$ and the reverse transformation, from aggregate to solid solution, at Ac_1 or $Ac_{3.2.1}$, imply structural changes of momentous importance to the steel metallurgist. While these will be dealt with at length in another lesson it seems proper to record here their significance. These structural changes give the key to the rational treatment of steel. They make possible the refining of steel by heat treatment seeing that on heating steel through its critical range we may change it from the condition of a coarse aggregate (a coarse structure) to the condition of a fine, nearly amorphous, solid solution. They also make possible the hardening of steel through sudden cooling from above the critical range as will be fully explained in another lesson.

Prevailing Conditions Above and Below the Critical Range. — The following condensed statement of some of the most significant conditions prevailing above and below the critical range of iron-carbon alloys may be useful in keeping these fundamental facts in mind. By critical range is, of course, meant here the critical points, both on heating and cooling, considered collectively and it will be understood that the conditions described as existing above the range change quite abruptly to the conditions prevailing below the range as the metal cools through the range, or vice versa as it is heated above it. The references made to the crystallizing of the metal and to the influence of work both above and below the range will be understood after reading the following lessons dealing with the treatment of steel.

Conditions and Properties of Iron-Carbon Alloys and of their Constituents

Above Critical Range	*Below Critical Range*
olid solution (austenite).	Aggregate (ferrite + cementite).
ardening (dissolved) carbon.	Cement carbon (Fe_3C).
amma iron.	Alpha iron.
lloys containing a sufficient amount of carbon possess hardening power.	Same alloys deprived of hardening power.
lloys are non-magnetic.	Alloys are magnetic.
etal crystallizes on slow cooling.	Metal does not crystallize on slow cooling.
ork prevents crystallization.	Work distorts structure.

Properties of Gamma, Beta, and Alpha Iron. — The various properties of gamma, beta, and alpha iron described in the preceding pages, have been tabulated below as well as some other data of interest. These are in accordance with the views most generally held, but the author is well aware that those entertaining different views may take exception to some of the entries.

	Gamma Iron	Beta Iron	Alpha Iron
Metallurgical name	Austenite	Beta ferrite	Ferrite, alpha ferrite, pearlite ferrite
Solvent power for C (or Fe_3C)	dissolves carbon up to 1.7 per cent or Fe_3C up to 25.5 per cent	probably some but opinions differ	probably none, but opinions differ
Range of temperature in which stable	above A_2, $A_{3\text{-}2}$, or $A_{3\text{-}2\text{-}1}$ in case of pro-eutectoid ferrite, above A_1 or $A_{3\text{-}2\text{-}1}$ in case of eutectoid ferrite	as free beta ferrite between A_3 and A_2	below A_3, $A_{3\text{-}2}$, or $A_{3\text{-}2\text{-}1}$
System of crystallization	cubic (orthorhombic according to Le Chatelier)	cubic	cubic
Prevailing crystalline forms	octahedra	cubes	cubes
Other crystalline characteristics	frequent twinnings	no twinnings	no twinnings
Specific gravity	greater than beta and alpha iron (dilatation at Ar_3)	greater than alpha iron (gradual dilatation at Ar_2, Osmond)	smaller than gamma and beta iron
Electric conductivity	ten times smaller than that of alpha iron at ordinary temperature	greater than that of gamma iron and increasing with falling temperature	greater than that of beta iron and increasing with falling temperature
Magnetic properties	non-magnetic	feebly magnetic	strongly magnetic
Hardness	softer than beta iron, harder than alpha iron	very hard	soft

Examination

I. Describe and discuss the change of properties occurring in steel containing 0.25 per cent carbon as it cools from a temperature exceeding its critical range to ordinary temperature.

II. Describe the changes of properties taking place at $Ar_{3\,2\,1}$.

LESSON X

CAST STEEL

The structural and other changes taking place at the thermal critical points of steel account for the deep changes of properties resulting from the treatments to which steel is subjected in the process of manufacture of steel objects. We are now in a position to understand these changes, to anticipate them, and to arrive at the rationale of the treatment of steel which for so many centuries remained purely empirical.

It is logical that we should first consider the structure of steel before it has received any treatment whatsoever, namely, the structure of the metal in its cast condition. To this study the present lesson will be devoted.

The structure of cast steel is different from what, in these lessons, has been termed the normal structure of the metal because, having been developed during very slow and undisturbed cooling from the molten condition, crystalline growth has been promoted, whereas in working and reheating such large growth is hindered or corrected. It may well be expected then that the structure of steel castings will be coarser, as is generally expressed, that is, made up of larger crystalline grains, than the normal structure so far considered, and therefore that steel castings will suffer from all the ills that pertain to a coarse structure, namely, weakness, lack of ductility, or even brittleness, etc. It will be profitable at the outset to consider in a general way the genesis of the structure of cast eutectoid, hypo-eutectoid, and hyper-eutectoid steel.

Structure of Cast Eutectoid Steel. — Let us first look into the genesis of the structure of eutectoid steel in the cast condition. Above its melting-point this steel, like all steels, consists of a liquid solution of carbon or of the carbide Fe_3C in iron (see Fig. 4, Lesson VIII). Upon solidifying this liquid solution is converted into a solid solution, that is, the carbon or carbide remains dissolved in the iron, known now as gamma iron. This solid solution of iron or carbide of iron in gamma iron is called austenite. Solidification means crystallization: crystals or crystallites of austenite form during the solidification and, as is usual, the slower the solidification the larger will the crystals be. Osmond has shown that these crystals belong to the cubic system and that they are chiefly octahedra (although this is doubted by Le Chatelier). These octahedra of austenite continue to grow on slow cooling below the solidification, this growth being effected through several adjacent crystalline grains taking the same orientation and therefore merging into a larger crystalline grain. It is evident, therefore, that in the process of making steel castings the slow and undisturbed cooling prevailing both during and after solidification promotes the formation of large grains of austenite, these grains being made up of small octahedric crystals, and that the larger the castings the larger generally the crystalline grains, that is, the coarser the structure. When slowly and undisturbedly cooled eutectoid steel then reaches its single critical

point, $A_{3.2.1}$, it is composed of relatively large grains of austenite. In passing through this point the austenite grains are converted bodily into as many pearlite grains, as explained in Lesson VIII, a coarse austenitic structure acquired at a high temperature giving rise to a coarse pearlitic structure at ordinary temperature. The polyhedric structure, therefore (Fig. 1), observed after complete cooling indicates the original polyhedric structure of austenite formed above the critical point. The meshes of the network are sections through pearlite grains, the net merely boundary lines between such grains, originally boundary lines between austenite grains. This polyhedric structure of slowly cooled steel proves the polyhedric structure of austenite at a high temperature. Because of a coarser grain and coarser pearlite cast eutectoid steel is weaker and less ductile than eutectoid steel properly worked or annealed or both.

Structure of Cast Hypo-Eutectoid Steel. — Let us now consider the genesis of the structure of hypo-eutectoid steel, and let us select as an example steel containing

Fig. 1. — Eutectoid steel. Cast. Magnified 500 diameters. (Boylston.)

Fig. 2. — Hypo-eutectoid steel. Cast. Free ferrite rejected chiefly to the boundaries. Magnified 100 diameters. (H. C. Cridland in the author's laboratory.)

0.60 per cent carbon and, therefore, composed after complete slow cooling of 72 per cent of pearlite and 28 per cent of free ferrite. The formation of the structure of this steel has been depicted in Figure 2, Lesson VIII, to which the reader is referred. This steel on solidifying passes, like all steels, from the condition of a liquid solution of iron and carbon to that of a solid solution of carbon (or more probably Fe_3C) in gamma iron, this solid solution, or austenite, being made up of crystalline grains. The austenite grains formed during solidification continue to grow as the steel cools slowly to its upper critical point $Ar_{3.2}$, when, as explained in Lesson VIII, ferrite begins to be liberated and continues to be liberated as the metal cools to its lower point Ar_1. This setting free of ferrite is apparently brought about by each grain of austenite rejecting the ferrite in excess of the eutectoid composition, so that by the time the point Ar_1 is reached each residual grain of austenite has the eutectoid composition and on cooling through Ar_1 is converted bodily into a grain of pearlite. Microscopical examination reveals the fact that the pro-eutectoid ferrite is rejected (1) to the boundaries of

the decreasing austenitic grains and (2) between the cleavage or crystallographic planes of these crystalline grains, so that three types of structures may be distinguished in cast hypo-eutectoid steel, (*a*) structures in which the free (pro-eutectoid) ferrite has been rejected chiefly to the boundaries of the austenitic grains (Fig. 2), clearly indicating that these grains were polyhedric, (*b*) structures in which the free ferrite has been rejected chiefly between the cleavage planes of austenite (Fig. 3), proving the crystalline character of that constituent and suggesting as later explained that its crystallization is cubic, and (*c*) structures in which the free ferrite has been rejected partly to the grain boundaries and partly between the cleavage planes. Long exposure to high temperatures followed by slow cooling appears to favor the massing of free ferrite between crystallographic planes, whereas short exposure

Fig. 3. — Hypo-eutectoid steel. Cast. Free ferrite rejected chiefly between cleavage planes. Magnified 100 diameters. (W. J. Burger, Correspondence Course student.)

and more rapid cooling promotes the expulsion of free ferrite to the grain boundaries, resulting in sharply defined network structures.

The structure of cast hypo-eutectoid steel is coarse (1) because its slow and undisturbed cooling promotes the formation of large austenite grains and hence, later, of large pearlite grains, (2) because its slow cooling between the upper and lower critical points favors the rejection of a maximum amount of free ferrite which rejection makes for coarseness of structure, and (3) because its slow cooling from the upper critical point to atmospheric temperature promotes the crystallization of free ferrite into large grains, this influence, however, being material only where there is a large amount of free ferrite, i.e. in very low carbon steel.

Because of its coarser structure cast hypo-eutectoid steel is less tenacious and less ductile than forged or properly annealed steel of similar composition.

Structure of Cast Eutectoid vs. Structure of Cast Hypo-Eutectoid Steel. — Although the pearlite grains of eutectoid steel may be and often are larger than the pearlite grains of hypo-eutectoid steel, the latter, especially when judged by its frac-

ture, is the coarser of the two. This greater coarseness of hypo-eutectoid spite of smaller pearlite grains is due to the presence of free ferrite, relativel pearlite grains surrounded by coarse ferrite envelopes or holding coarse ferrite p imparting a coarse appearance to the fracture of steel. The dimension of the grains, therefore, while not without influence, is not the criterion by which t of the coarseness or fineness of the structure and fracture of hypo-eutectoid st amount of free ferrite present and its mode of distribution having to be tal consideration. In very low carbon steel, moreover, there is but little pear the small amount present occurs as small irregular particles (Fig. 4) exerting b influence upon the character of the fracture which now depends quite exclusive the dimension of the ferrite grains. As ferrite grains, however, no matter ho never impart as fine a structure or fracture to steel as pearlite grains, it follo

Fig. 4. — Hypo-eutectoid steel. Cast. Carbon 0.20%. Magnified 28 diameters. (Boylston.)

low carbon (ferritic?) steels can never have as fine a structure or fracture as carbon (pearlitic) steels.

Structure of Cast Hyper-Eutectoid Steel. — The genesis of the structure hyper-eutectoid steel has been depicted diagrammatically in Figure 3, Lesso Between its solidification point and its upper critical point (A_{cm}) this steel i posed, like all steels, of crystalline austenite grains formed on solidifying and quent slow cooling. Upon reaching the point Ar_{cm} the setting free of ce begins, ending only at the lower point $Ar_{3.2.1.}$ This free cementite, like the free of hypo-eutectoid steel, is rejected (1) to the boundaries of the diminishing au grains and (2) between the cleavage planes of this crystalline austenite, givi to the three types of structure described in the case of hypo-eutectoid steel, which free ferrite is replaced by free cementite, namely, (*a*) structures in which t cementite is found chiefly at the grain boundaries, (*b*) structures in which t cementite is chiefly located between cleavage planes, and (*c*) structures in wh free cementite is partly at the boundaries and partly between crystallo

planes (Fig. 5). Like the structure of cast hypo-eutectoid steel, the structure of cast hyper-eutectoid steel bears witness (1) to the polyhedric form of the austenite grains, (2) to the crystalline character of these grains, and (3) to their probable cubic crystallization.

Long exposure to high temperatures followed by very slow cooling promotes in hyper-eutectoid steel the rejection of cementite to the cleavage planes, while short exposure and more rapid cooling favor the rejection of cementite to the boundaries.

The rejection of free cementite like the rejection of free ferrite makes for coarseness of structure and fracture, from which it follows that cast and slowly cooled hyper-eutectoid steel will be coarser than cast and slowly cooled eutectoid steel, and that the more free cementite it contains, that is, the higher the carbon, the coarser it will be. The structure and fracture of hyper-eutectoid steel, however, will generally be

Fig. 5. — Hyper-eutectoid steel. Cast. Free cementite rejected partly to the boundaries and partly between cleavage planes. Magnified 114 diameters. (Boylston.)

decidedly finer than that of hypo-eutectoid steel because of the very small amount of free cementite present in the former compared to the amount of free ferrite in the latter, unless, indeed, the hypo-eutectoid steel be very near the eutectoid composition. This is due to the fact, now well understood, that starting from the eutectoid composition (carbon 0.85 per cent), as the carbon decreases the amount of free ferrite increases rapidly, while as the carbon increases above the eutectoid ratio the amount of free cementite increases slowly and remains small even with high carbon content. Steel with 0.50 per cent carbon, for instance, contains 40 per cent of free ferrite, hence its coarseness both of structure and fracture, while steel with say 1.25 per cent carbon contains but 6.4 per cent of coarsening free cementite, hence the relative fineness of both its structure and fracture.

Ingotism. — Howe has suggested the term "ingotism" to designate the structure of cast steel described in the foregoing pages and characterized (1) by large pearlite grains and (2) by coarse ferrite or cementite membranes surrounding them and by irregular masses of these constituents located in some of the cleavage planes of the original austenite grains.

ture, is the coarser of the tw
spite of smaller pearlite grai
pearlite grains surrounded by
imparting a coarse appearanc
grains, therefore, while not
of the coarseness or fineness
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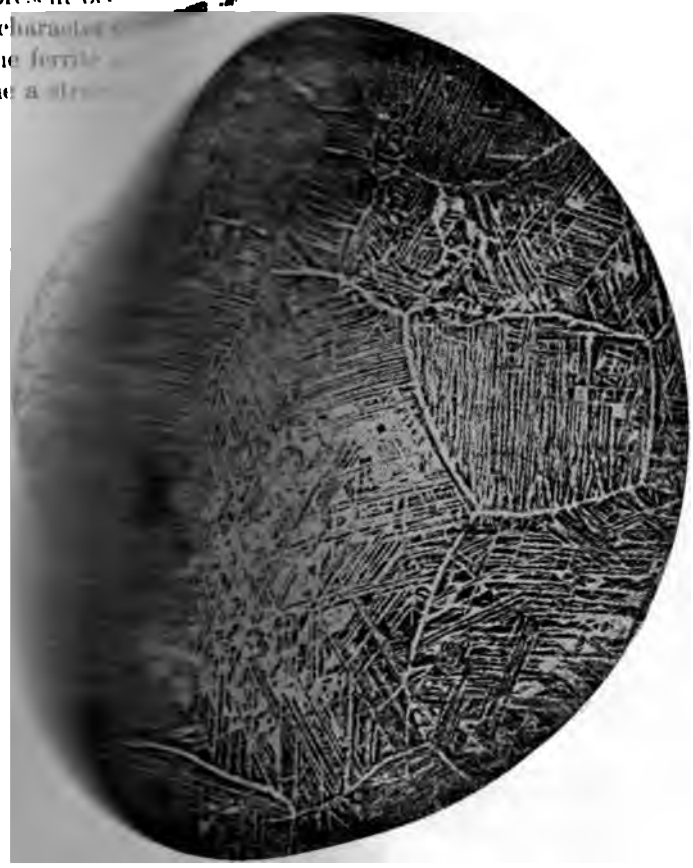

Fig. 1. Steel containing 0.55 per cent carbon. Widmanstätten structure. Magnified 6 diameters. (Belaiew.)

low carbon
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... when it is considered that the conditions required for
... are greatly exaggerated and intensified during the
... a very slow solidification peroid, (2) very long expo
... very slow cooling from these high temperatures.
... a remarkable manner in reproducing the Widmanstä
... steels to a high temperature for a very long time
... slowly, the fall of temperature from 1500 to 300 deg. C.
... attempt at reproducing the conditions which must pre
... and further cooling of meteorites. The structures obta
... steel containing 0.55 per cent carbon and otherwise of

mercial quality are shown in Figures 6, 8, 10, 12, and 13. They are typical structures of steel castings of the same grade but on a much larger scale for it should be noted that the magnification of Figures 8, 10, 12, and 13 is only 30 diameters while Figure 6 is magnified but 6 diameters. Figure 6 is a beautiful illustration of that

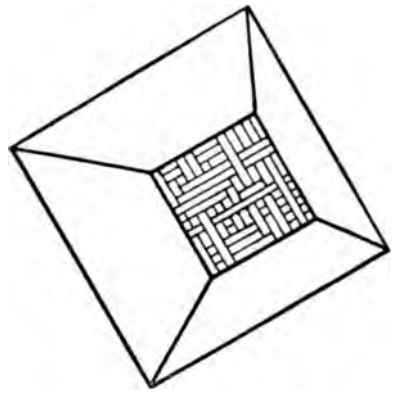

Fig. 7. — Section parallel to the surface of a cube. (Tschermak).

Fig. 8. — Steel. Carbon 0.55%. Section parallel to the surface of a cube. Magnified 30 diameters. (Belaiew.)

type of structure in which the free ferrite has been rejected both to the grain boundaries forming a sharply outlined network and between crystallographic planes. In Figures 8, 10, 12, and 13 the free ferrite is seen massed between cleavage planes.

Octahedric Crystallization of Austenite. — It will be noted that the ferrite bands shown in Figures 8, 10, 12, and 13 cut each other at right angles or, more frequently, form equilateral triangles. According to crystallographers these are indications that austenite crystallizes in regular octahedra. That this inference is correct appears to be conclusively proven by the following remarks of Belaiew.

"Let us consider an octahedron and let us assume that four systems of lamellæ locate the in this octahedron along its crystallographic planes, that is, parallel to the four pairs of its s a fact that has been long known in the case of meteoric irons.

"If we now examine any section of the octahedron, we shall find that not only the angles by the projections of the lamellæ vary in different sections, but that the number itself of

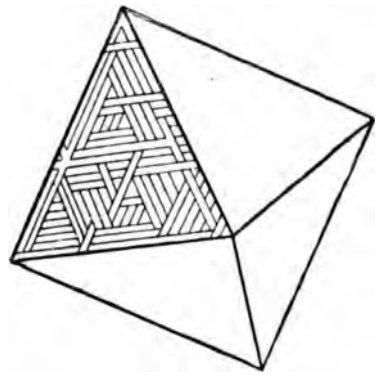

Fig. 9. — Section parallel to the surface of an octahedron. (Tschermak.)

Fig. 10. — Steel. Carbon 0.55%. Section parallel to the surface of an octahedron. Magnified 30 diameters. (Belaiew.)

sections varies likewise from two to four. For instance, when the section is parallel to the of the cube, the number of different sections is minimum, that is, two, and in the entire se find only two systems of lamellæ forming right angles. Figure 7 is a diagram of such and Figure 8 a corresponding section of the steel.

"A section parallel to one of the surfaces of the octahedron will yield equilateral triangles by three systems of lamellæ forming 60° angles; the fourth system coincides with the sect sidered (see Figs. 9 and 10).

"In a section parallel to the surface of the dodecahedron, two systems of lamellæ are observed forming an angle of 109° 28′ 16″; the other two systems coincide and divide this angle in half (Figs. 11 and 12). Finally any section will give four different systems cutting each other at different angles (Fig. 13).

"All these cases, as we have just seen, can very well be illustrated by different samples of our

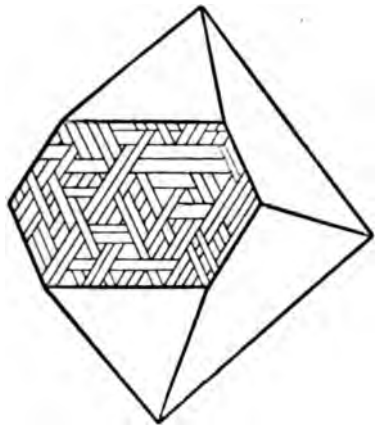

Fig. 11. — Section parallel to the surface of a dodecahedron. Magnified 30 diameters. (Tschermak.)

Fig. 12. — Steel. Carbon 0.55%. Section parallel to the surface of a dodecahedron. Magnified 30 diameters. (Belaiew.)

alloy which, firstly, affords a rather weighty proof of the octahedric crystallization of steel and, secondly, brings out the remarkable analogy of this structure with that of meteorites and warrants us to allude to the synthesis of the structure so called of Widmanstätten . . . this structure is the necessary consequence of the uniform orientation of the elementary octahedra within a volume of greater or less dimension; it is, therefore, in no way related with the carbon content and must be

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ation

of (1) cast hypo-eutectoid steel, (2)
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LESSON XI

THE MECHANICAL TREATMENT OF STEEL

Forged steel objects are manufactured by subjecting the cast metal (1) to pressure exerted by rolls, presses, or dies, or to blows from hammers and (2) by reheating it to various temperatures for various lengths of time and cooling it at various rates. In other words we have to consider (1) the mechanical treatment of steel and (2) its heat or thermal treatment. The machining of steel is not here mentioned since it can evidently have no effect upon the structure and properties of the metal, unless it be a very superficial one.

While the primary purpose of working steel is to shape it into useful appliances and while the primary purpose of reheating it may be, and often is, to impart to the metal such plasticity as will facilitate its being so shaped, both mechanical and heat treatments deeply affect the structure of steel and therefore its physical properties. To this very important subject the next four lessons will be devoted. We shall first consider the influence of mechanical treatment and then that of heat treatment.

The effect of work upon the structure and properties of steel greatly depends upon the temperature of the metal while it is being worked, the expressions "hot working" and "cold working" being common ones, the former meaning working the steel while hot, and the second working it while cold, more specifically at atmospheric temperature. In these lessons the expression hot working will be applied to working the metal while above its critical range, and cold working to work performed below that range. In justification of this course it will be shown that the effect of work changes quite sharply as the critical temperature of steel is passed.

Hot Working. — Hot working may be applied to steel (1) after it has solidified but before it has cooled to a much lower temperature so that it still possesses the necessary plasticity, or (2) the steel ingot may be allowed to cool to atmospheric temperature or at least to a temperature so low that reheating is required as a preliminary step to successful hot working. The following considerations will show that so far as the influence of hot work is concerned it is quite immaterial whether the steel ingot has or has not been completely cooled before being brought to the forging temperature. Let us assume that the steel ingot be allowed to cool to atmospheric temperature, that it is then reheated to a temperature well above its critical range and then subjected to hot working.

An attempt has been made in Figure 1 to depict graphically the influence of hot work on the structure of steel. The diagram will be readily understood. The critical range both on heating and cooling is represented by a double line, but the reader will, of course, bear in mind that the critical range on heating does not coincide with the range on cooling and that each range may include one, two, or three critical points, as fully explained in previous lessons. For the present purpose it is preferable to present both ranges irrespective of the number of critical points included by the two parallel lines shown in the diagram. The solidification range is likewise indicated by a double line. The widths of the shaded areas are intended to be propor-

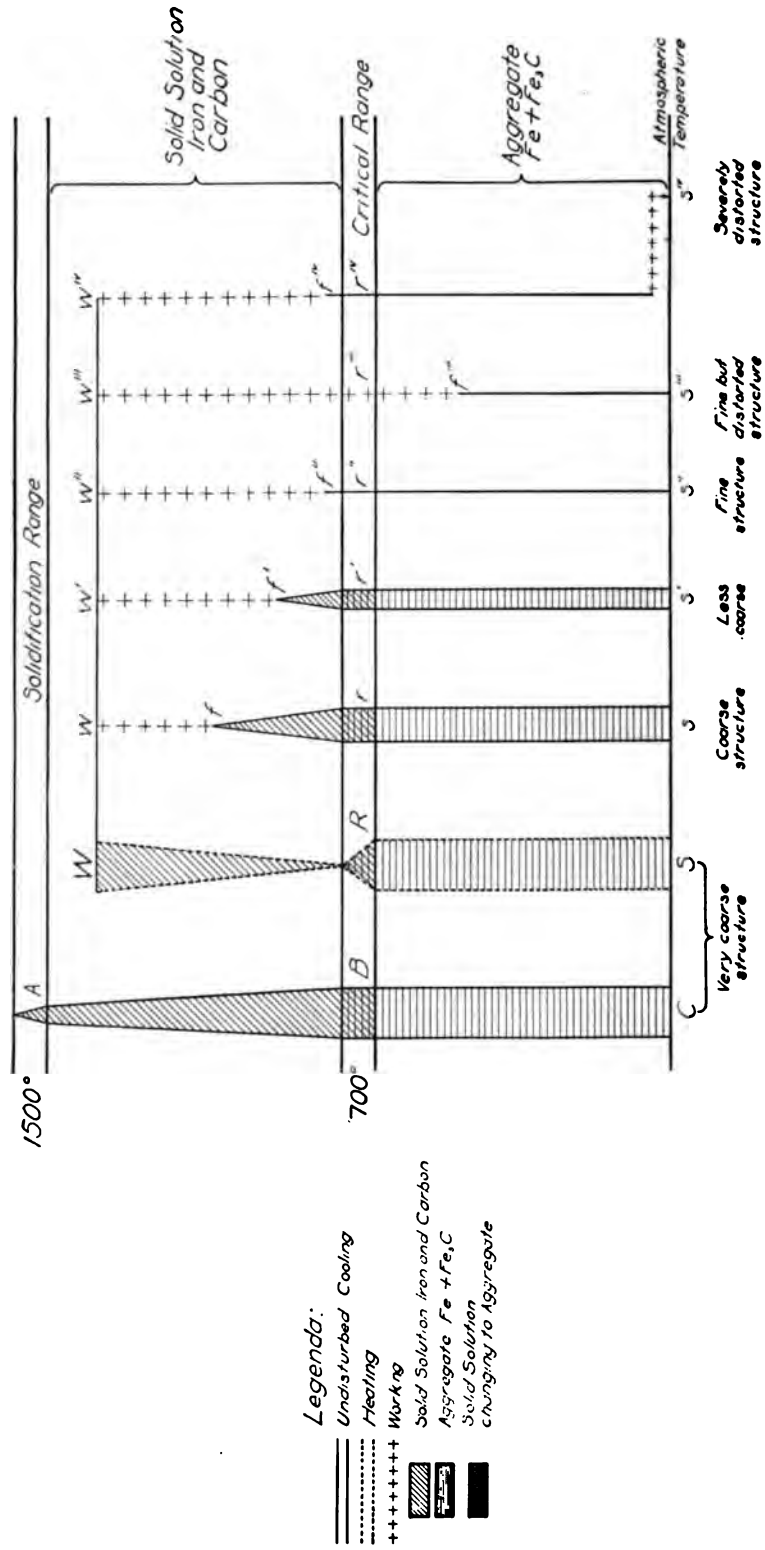

Fig. 1. — Diagram depicting the influence of work upon the structure of steel.

ional to the grain size resulting from the various treatments; when an area is reduced to a mere line the corresponding grain is very small, i.e. the structure very fine. As the steel ingot solidifies at *A* crystalline grains are formed which increase in size on slow and undisturbed cooling to the critical range *B*. In passing through that range the austenite grains are converted into pearlitic grains with or without rejection of free ferrite or of free cementite according to the carbon content of the steel. On cooling from *B* to *C* there is no further growth and the size of the final grain may be represented by the width of the shaded area at *C*. The metal has now the usual coarse structure of steel castings described in Lesson X. Upon reheating this coarsely crystalline steel ingot from *S* to *R* and through its critical range, it is converted from the condition of an aggregate of ferrite and cementite into a nearly amorphous solid solution, so that as the metal emerges from its range it has a very fine structure. As steel just above its critical range, however, would not be plastic enough for hot working and would not afford the necessary range of temperature through which to cool while being worked and still remain, as it should, above the range, it is generally necessary to heat the metal to a much higher temperature, say to some 1200 deg. C. or even more (*W* in Fig. 1). As the metal is heated from its critical range to this high temperature, it probably crystallizes so that when work begins at *w* it is in a somewhat crystalline condition. This grain growth on heating from *R* to *W* is depicted in the diagram. The heavy pressure or blows which are now applied, however, soon break up this crystallization while preventing a new one from forming, so long at least as the work continues sufficiently vigorous, for *undisturbed* cooling is a condition necessary for the ready growth of crystals. As soon as work ceases, however, the metal being now left to cool undisturbedly, if its temperature is then above its critical range, for instance at *f*, it will immediately begin to crystallize and its crystallization will continue from *f* to *r*, that is, until its critical range is reached, when it will stop and the austenite grains just formed will be converted into as many pearlite grains with or without rejection of free ferrite or free cementite. The width of the band at *s* is intended to represent the size of the final grain. It is smaller than the grain of the steel ingot but it is still large.

If work ceases, then, while the metal is still above its critical range it is evident that it will crystallize and that the resulting grains will be the larger, that is, its structure will be the coarser, the higher the temperature at which the work was stopped.

Finishing Temperatures. — The temperatures at which work ceases are known as the finishing temperatures and the above considerations will show the importance of proper finishing temperatures if it be desired to impart to steel implements the finest grain that it can acquire through working together with the desirable properties inherent to it.

Should hot work be continued, for instance, until the temperature of the metal is but slightly above its critical range, *f'* in Figure 1, the austenitic grains that will form on undisturbed cooling to the range will be small, so that the final grain of the metal at *s'* will likewise be small, as indicated by the width of the shaded area. If the finishing temperature is exactly at the critical range, *f''*, the final grain at *s''* will be very fine. If working be continued until the metal has cooled to a temperature lower than its critical range, for instance *f'''* in the diagram, the structure will be fine since crystallization was prevented while the metal was cooling above its critical range, but it will be distorted because the effect of working below the range, that is,

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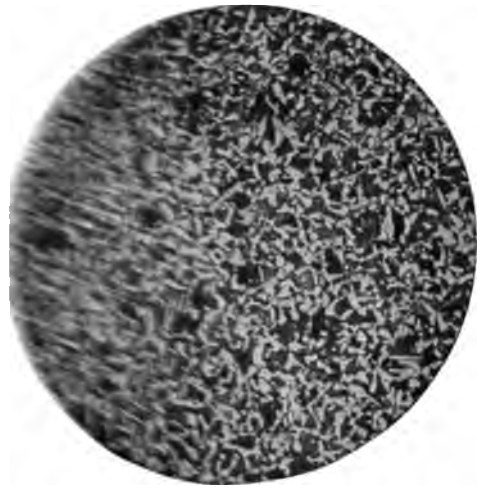

... hypo-eutectoid steel.
... Finishing temperature near
... Magnified 100 diameters.
... Correspondence Course student.)

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Hypo-Eutectoid Steel. — If hypo-eutectoid s
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... consists of particles of pearlite embedded in a

If the working of hypo-eutectoid steel ceases at a temperature considerably above its critical range, *f* in Figure 1, the austenite grains formed on cooling to the range will be relatively large and therefore also the pearlite grains of the completely cooled

Fig. 3. — Hot worked hypo-eutectoid steel. Carbon 0.05%. Magnified 114 diameters. (Boylston.)

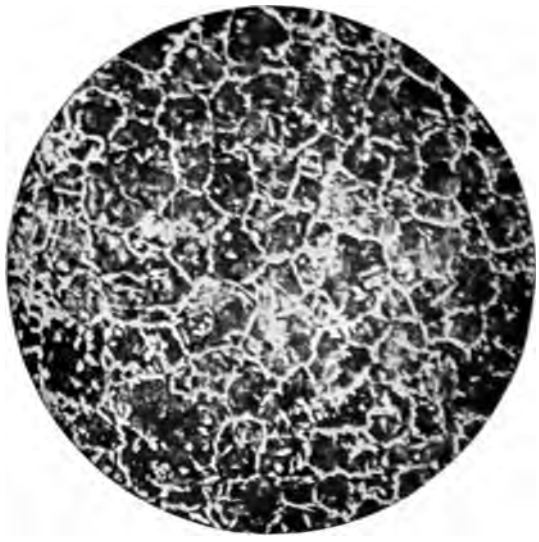


Fig. 4. — Hot worked hypo-eutectoid steel. Carbon 0.50%. Finishing temperature considerably above the critical range. Magnified 56 diameters.

metal. The free ferrite will still be found chiefly at the boundaries (Fig. 4), the meshes of the network structure, however, being larger than in similar steel finished at a lower temperature, as will be apparent from a comparison of Figures 2 and 4.

It will be seen that in forged hypo-eutectoid steel forming network structures on slow cooling through the critical range a close relation must exist between the size of the meshes and the finishing temperature.

Structure of Hot Worked Hyper-Eutectoid Steel. — If hyper-eutectoid steel be hot worked until its temperature is very near its critical range (*f''*, Fig. 1) and then allowed to cool undisturbedly, small austenite grains are formed which on cooling through the range are converted into small pearlite grains with rejection of free cementite, as shown in Figure 5. If the work be stopped at a temperature considerably above the critical range (*f*, Fig. 1), the final pearlite grains will be larger while the free cementite will be located chiefly at the grain boundaries, a network structure being produced. It will be evident that a close relation exists between

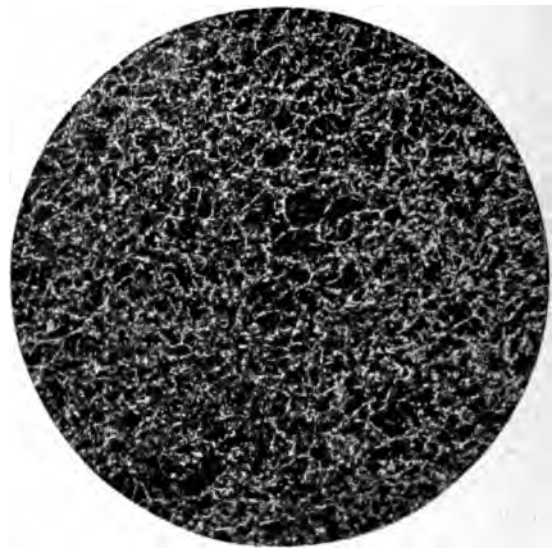


Fig. 5. — Hot worked hyper-eutectoid steel. Carbon 1.50%. Finishing temperature near critical range. Magnified 100 diameters. (Reinhardt in the author's laboratory.)

the size of the meshes of these network structures and the corresponding finishing temperatures.

Sorbite. — High magnification of the structure of the meshes of both hypo- and hyper-eutectoid steel described in the foregoing pages often fails to reveal the characteristic features of pearlite, namely, (1) sharply defined parallel plates alternately of ferrite and cementite and (2) a constant or nearly constant carbon content. The structure of these meshes instead remains indistinct and presents a granular rather than a lamellar aspect (Fig. 6). It is also frequently noted in connection with these network structures that the full amount of free ferrite or of free cementite has not been rejected, the pearlitic grains having retained some of the constituent in excess of the eutectoid ratio. To this imperfectly developed pearlite the name of sorbite has been given (Osmond) and quite universally adopted in spite of recent and regrettable efforts to eliminate it from metallographic nomenclature. It will be apparent that the formation of sorbite results from a relatively quick cooling through the critical

range, time being denied for the crystallization of distinct lamellæ of ferrite and cementite, and, in the cases of hypo- and hyper-eutectoid steel, for the rejection of the full amount of free ferrite or free cementite. The cooling in air of hot worked pieces, especially when of small size, is often sufficiently rapid to cause the formation of sorbite rather than of pearlite.

The production and nature of sorbite will be dealt with at greater length in another lesson. It should be mentioned here, however, that while sorbite is less ductile than pearlite it has a higher tenacity, higher elastic limit, and greater hardness (hence greater wearing power). When these qualities are required, in hot forged objects, they may consequently be obtained, although necessarily at the sacrifice of some

Fig. 6. — Hypo-eutectoid steel. Carbon 0.50%. The ill-defined constituent is sorbite. Magnified 1000 diameters. (Boynton.)

ductility and softness, by hastening the cooling through the critical range, after work has ceased, when sorbitic rather than pearlitic steel will be produced.

Hot Working of Steel vs. Its Critical Range. — In conducting the hot working of steel so as to impart to the metal the finest grain that can result from finishing at suitable temperatures, it is generally necessary only to consider its lower critical point on cooling, namely, Ar_1 or $Ar_{3\text{-}2\text{-}1}$. The following considerations will justify this statement. In the case of hypo-eutectoid steel if the working be continued while the metal cools from its upper point or points to its lower point, it will make for fineness of structure by preventing a coarse massing of the free ferrite while the cold working of that constituent, if taking place at all, must be very slight. The same reasoning applies, with greater force, to the hot working of hyper-eutectoid steel from its upper point (denoting the formation of free cementite) to its lower point $Ar_{3\text{-}2\text{-}1}$. Greater fineness of structure will result with very little, if any, distortion of the free cementite.

It is apparent, therefore, that in order to secure the finest grain obtainable through

mechanical refining without appreciable structural distortion steel objects should be finished slightly above their lower critical point, that is, in the vicinity of 700 deg. C. for all grades of commercial carbon steel.

Cold Working. — By the cold working of steel is meant in these pages the working of it while its temperature is below its critical range. It will now be shown that the effect of cold working upon the properties of the metal is very different from that of hot working. This should not be a cause for surprise if it be borne in mind that steel above its critical range is in a condition totally different from its condition below it. Above the critical range we have to deal with a solid solution of iron and carbon, below it with an aggregate of ferrite and cementite. The solid solution existing above the range will crystallize if allowed to cool undisturbedly and it has been shown in the foregoing pages that working in this range, i.e. hot working, is effective

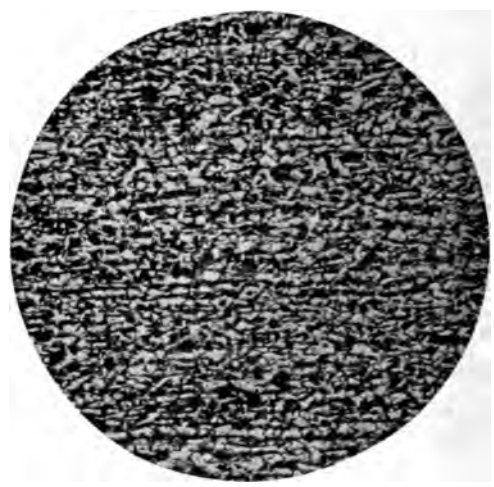


Fig. 7. — Cold worked hypo-eutectoid steel. Carbon 0.30%. Magnified 100 diameters. (Burger, Correspondence Course student.)

in preventing or at least retarding this crystallization, thus imparting a smaller grain to the metal. The aggregate of ferrite and cementite existing below the range, on the contrary, exhibits no tendency to crystallize during slow and undisturbed cooling, because this aggregate was formed and fully developed while passing through the range, the size of its elements, that is, its coarseness depending (1) upon the coarseness of the solid solution immediately before its transformation and (2) upon the time occupied in cooling through the range. Working this aggregate, therefore, as it cools to atmospheric temperature, or working it while at atmospheric temperature, i.e. cold working steel, does not prevent its crystallization. Its effect consists in *distorting* the existing aggregate structure, chiefly through the stretching or elongation of its crystalline elements (free ferrite, free cementite, pearlite) in the direction of the forging, and such distortion in turn means decreased ductility and eventually extreme brittleness. The effect of cold working upon the structure of steel is illustrated in Figures 7 and 8 in the case of hypo-eutectoid steel. It is also depicted in the diagram of Figure 1. While the structural distortion caused by cold working is very slight near the critical range of the metal, it rapidly increases as the temperature decreases,

ng very pronounced at atmospheric temperature. The manufacture of wire by awing affords a familiar instance of the effect of work performed at atmos- temperature both on the structure and properties of the metal. It is well that after the wire has been passed through several dies it becomes so brittle nealing is necessary in order to make further reduction in size possible, the ng operation removing the structural distortion and brittleness produced by g at atmospheric temperature.

chanical Refining. — It would seem as if with the use of pyrometers at least it be a relatively simple matter to finish steel objects very near the desirable

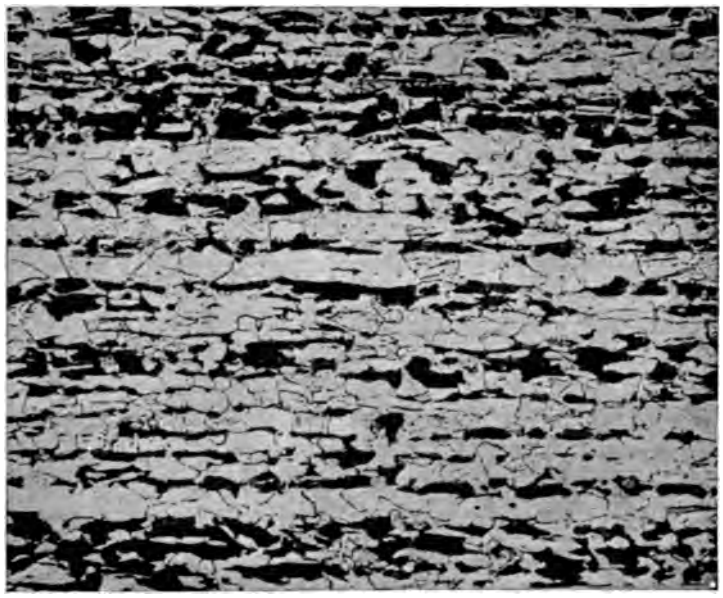


Fig. 8. — Cold worked hypo-eutectoid steel. Carbon 0.30%. Magnified 150 diameters. (Buck, Correspondence Course student.)

ature and thus secure for them the best structure that can be imparted by lone. Upon reflection, however, it will be manifest that the problem is on the y an insoluble one, for the reason that unless the objects are of very small ections, it is quite impossible to finish them so that their temperature will be n throughout, the central portions being necessarily hotter than the outside. the forging be so conducted that the temperature of the outside be very near tical range, the center, being materially hotter, will coarsen on cooling, while if plements, on the contrary, are finished so that their center may have the fine re produced by ceasing the work at the proper temperature, their outside must rily suffer from cold working. The limitations of work alone as a means of ing the best possible structure to steel are therefore quite evident.

ile a uniformly fine grain cannot be imparted to steel objects of considerable rough hot working alone, the value of hot work as a means of refining the re of steel remains very great as exemplified by the structure of properly hot steel when compared with the structure of steel castings of similar composi- The finer grain imparted to steel by working it has been called by some writers

"mechanical" refining to distinguish it from the refining produced by heat, i.e. from "thermal" refining. In practise hot work should be so conducted, that is, the finishing temperatures so regulated, that the central portions of the finished implements will not suffer unduly from the coarsening influence of too high a finishing temperature, while at the same time the outside will not suffer unduly from the effect of cold working. The natural tendency of rolling and other forging mills is to finish work at too high temperatures for the simple reason that the metal is then more plastic and consequently requires less power for its working. In some manufactures, however, and, especially in the rolling of rails, the importance of proper finishing temperatures has been given careful attention and the rolling operation so modified as to deliver rails of much finer grain and therefore better physical quality, than formerly.

Besides its important grain refining influence hot work further improves the quality of steel by closing and, if the carbon be low enough, welding, the blow-holes and otherwise increasing its soundness and by removing cooling strains.

Experiments

The student should prepare for microscopical examination samples of hot forged hypo-eutectoid, eutectoid, and hyper-eutectoid steel. Their structure should be compared with the structure of similar steels in the cast condition (Lesson X) and also with the structure of similar normalized steels (Lessons IV and V). If the forging of these samples was finished at a fairly high temperature their structure should be quite similar to the normal structure of like steels described in Lessons IV and V. Finer structures point to lower finishing temperatures.

A sample of cold worked steel preferably the longitudinal section of an unannealed cold drawn wire should likewise be prepared and its structural distortion noted.

If a cross-section of a rail or of some other rolled shape can be obtained, a piece should be cut from the center and one near the edge (advisably also from the web and extremity of flange in the case of a rail section). These pieces should be prepared and examined and the coarser grain of the central portion noted.

All specimens should be photographed preferably under a magnification not exceeding 100 diameters.

Examination

Describe briefly the effect upon the structure of steel (1) of working above the critical range (hot work) and (2) of working below that range (cold work).

LESSON XII

THE ANNEALING OF STEEL

Purpose of Annealing. — The purpose of annealing steel may be (1) to increase its softness and ductility that it may, for instance, be more easily machined or (2) to secure a desirable combination of high strength and elastic limit with fair ductility that it may successfully stand the strains to which it is to be subjected. These changes of physical properties result from corresponding changes in the structure of the metal brought about by proper heat treatment. In annealing steel it is generally intended to impart to it as fine a structure, that is as small a grain, as is consistent with the nature of the treatment and the grade of the steel. Hot forged steel objects may be improved by annealing for certain purposes, because of their structure being often (1) relatively coarse owing to high finishing temperature and (2) heterogeneous as explained in Lesson XI. The structure of cold worked steel, at least when severely cold worked, is so defective that the metal must be annealed before it can be put to useful purposes. Finally, steel castings have so coarse a structure as to be very deficient both in strength and ductility and should always be refined by annealing.

Nature of the Annealing Operation. — The annealing operation comprises three distinct steps: (1) heating the steel, (2) keeping its temperature constant at the annealing temperature, and (3) cooling it from the annealing to atmospheric temperature. These steps will be considered separately.

Heating for Annealing. — The first step in annealing always consists in heating the metal past its critical range because by so doing the preexisting structure, however coarse, is obliterated; the metal, for the time being, assuming a nearly amorphous structure. This important structural change is due, as we now understand it, to the passage of the steel from the state of an aggregate of ferrite and cementite to that of a homogeneous solid solution, and it is not to be wondered at that so radical a structural change should destroy effectively any preexisting crystallization. The annealing of steel castings, however, constitutes an apparent exception to the rule that heating just through the range is sufficient to break up effectively the preexisting structure, for their successful annealing often requires a materially higher temperature. Should the temperature of the steel remain below its critical range, no structural change would take place and the annealing would be ineffective (I, Fig. 1).[1] Should, on the contrary, the temperature of the steel be carried considerably above the range, its structure, which was finest as it emerged from the range, begins to coarsen on further heating and continues to grow as the metal cools slowly to the range, so that its final structure would be at least relatively coarse (II, Fig. 1). Clearly, therefore, to an-

[1] When steel contains hardening carbon it may be softened and made more ductile by heating it to temperatures lower than its critical range (as in the tempering of hardened steel) but such treatment is not, or at least should not be, called annealing. Cooling strains may also be removed, at least in part, by heating below the range.

neal steel forgings they should be heated through their critical range and kept at a temperature as close to the upper part of that range as possible (III, Fig. 1). The annealing temperature will, of course, vary with the carbon content since the position of the critical range, or rather its width, varies likewise. The following ranges of temperatures are recommended by the Committee on Heat Treatment of the American Society for Testing Materials. The report of the Committee states that for steels containing more than 0.75 per cent manganese slightly lower temperatures suffice.

Range of Carbon Content	Range of Annealing Temperature
Less than 0.12 per cent	875 to 925 deg. C. (1607–1697 deg. F.)
0.12 to 0.25 per cent	840 to 870 deg. C. (1544–1598 deg. F.)
0.30 to 0.49 per cent	815 to 840 deg. C. (1499–1544 deg. F.)
0.50 to 1.00 per cent	790 to 815 deg. C. (1454–1499 deg. F.)

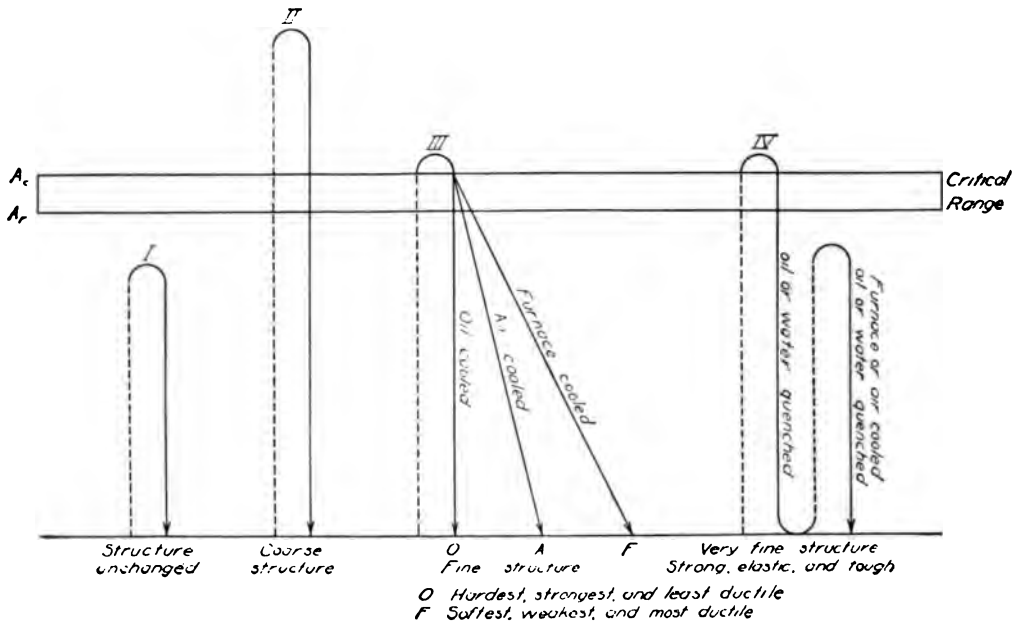


Fig. 1. — Diagram depicting the annealing of steel.

Time at Annealing Temperature. — The steel object should be kept at the annealing temperature long enough to be heated right through to that temperature. The Committee on Heat Treatment, referred to above, states that an exposure of one hour should be long enough for pieces twelve inches thick. Thicker pieces, of course, need a longer heating.

The usefulness of pyrometers in conducting annealing operations is obvious. Their use is to be strongly recommended.

Cooling from Annealing Temperature. — Having imparted a fine structure to the steel the next step must be to retain it. The most effective way of accomplishing this consists in cooling the steel very quickly, by quenching it in water for instance, as time is then denied for the structure to coarsen at all while the metal cools to atmospheric temperature. Such rapid cooling, however, as is well known, hardens the metal and deprives it of ductility (unless, indeed, it contains very little carbon), and

this would defeat the purpose of annealing which always demands the retention of considerable ductility. It follows from these considerations that, in annealing, cooling from the annealing temperature cannot be so rapid as to very materially harden the steel. Its rate should, moreover, be regulated in accordance with the kind of properties we most desire the steel object to possess. For instance, (1) if softness and ductility are wanted (for ease in machining), necessarily at a certain sacrifice of strength and elasticity, the cooling should be very slow, to wit, with the furnace in which the object was heated, (2) if greater hardness (for wearing power), strength, and elasticity are desired, at the necessary sacrifice of some ductility, the cooling should be more rapid as, for example, in air or, in the case of low carbon steel, in oil or, with very low carbon steel, even in water (III, Fig. 1).

Rate of Cooling vs. Carbon Content. — The lower the carbon content the more rapid may be the cooling from the annealing temperature without affecting too deeply

Fig. 2. — Steel. Carbon 0.50 per cent. Magnified 100 diameters. Heated to 1000 deg. C. and slowly cooled in furnace. (W. J. Burger, Correspondence Course student.)

the ductility of the metal. For instance, (1) steel containing not over 0.15 per cent carbon may be quenched in water, thereby increasing its strength and elastic limit and still remain very ductile, (2) steel with less than 0.20 or 0.30 per cent carbon may be quenched in oil with satisfactory results, (3) with a larger proportion of carbon such rapid cooling is no longer possible, as it would destroy the ductility of the metal, recourse having then to be had to cooling in air for the desired combination of strength and ductility or to the double annealing treatment soon to be described.

Rate of Cooling vs. Size of Object. — Since large objects necessarily cool more slowly than smaller ones when subjected to the same cooling influences, it is evident that the external conditions should also be regulated in accordance with the dimensions of the objects treated. To secure maximum softness and ductility, for instance, the cooling of small objects should be more effectively retarded than the cooling of larger ones. Assume, for example, two objects made of the same steel, one large and one small, and both cooled in air from the annealing temperature; the smaller object

will be harder and less ductile than the larger one, because of its quicker cooling. To render it as soft and ductile as the larger object cooling in the furnace may be necessary. Similarly, to give strength and high elastic limit the cooling of large objects must be more vigorously hastened than that of smaller objects as, for instance, cooling in oil against cooling in air for the smaller piece.

Furnace Cooling from Annealing Temperature. — As an example of the effect of furnace cooling upon the structure of steel, let us take a steel bar ½ in. square, containing 0.50 per cent carbon, heated to 1000 deg. C. and slowly cooled with the furnace. Its structure is shown in Figures 2 and 3. It will be seen to be composed of the normal proportions of pearlite and free ferrite, namely, some 60 per cent of the former, and it will also be noted that the pearlite is distinctly laminated (Fig. 3),

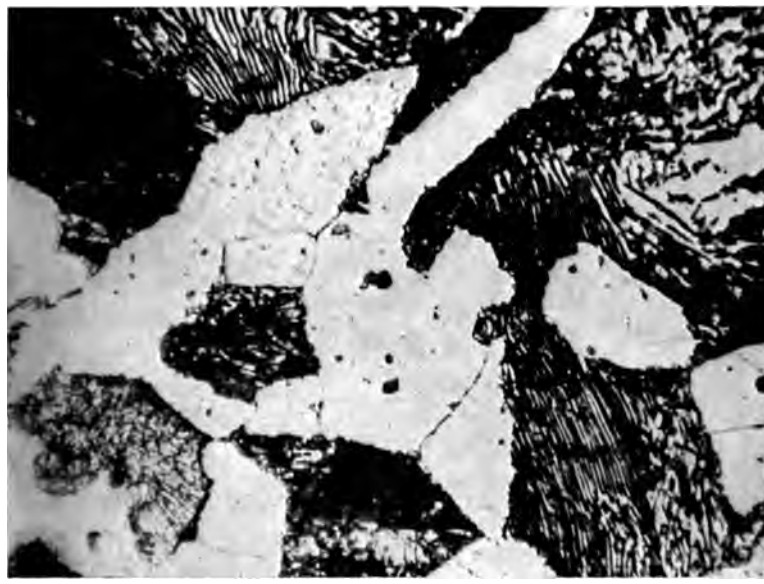


Fig. 3. — Steel. Carbon 0.50 per cent. Magnified 670 diameters. Heated to 1000 deg. C. and slowly cooled in furnace. (C. C. Buck, Correspondence Course student.)

and that in places at least the ferrite forms characteristic polyhedric grains. This structure is due to the slow cooling of the steel through its critical range, which permits the rejection of the full amount of free ferrite and a distinct crystallization of the constituents of the residual austenite into plates of ferrite and cementite. The relative softness and great ductility of the steel in this condition is due (1) to the presence of the full amount of soft ferrite in relatively large areas and (2) to the presence of distinctly laminated pearlite indicating the absence of hardening carbon as explained later.

Air Cooling from Annealing Temperature. — To illustrate the influence of air cooling upon the structure of steel, let us take likewise a steel containing some 0.50 per cent carbon, heated to 1000 deg. C. and cooled in air. Its structure is shown in Figure 4. It will be found quite unlike the structure of the same steel after furnace cooling (Figs. 2 and 3). It contains a much smaller proportion of free ferrite, apparently not over 20 per cent, in the form of a distinct net surrounding dark meshes

which a high magnification fails to resolve into distinct parallel plates. Relatively quick cooling through the critical range has prevented the separation of the normal amount of free ferrite, from which it necessarily follows that the dark constituent contains more ferrite than true pearlite; nor has it the structure of true pearlite, time also having been denied on cooling through the range for the formation of distinct plates of ferrite and cementite. Sorbite is the name of this constituent. The structure of pearlite passing into sorbite is shown in Figure 5.

Properties of Sorbite. — Sorbite has already been briefly described in Lesson XI, where it was shown that it could be produced in steel forgings of small sections through simple air cooling from a finishing temperature superior to the critical range,

Fig. 4. — Steel. Carbon 0.50 per cent. Magnified 100 diameters. Heated to 1000 deg. C. and cooled in air. (W. J. Burger, Correspondence Course student.)

and in larger sections by hastening somewhat their cooling through that range. It has also been stated that sorbite is harder, stronger, and less ductile than pearlite. By so regulating the cooling from the annealing temperature, therefore, that sorbitic steel is produced, hardness, strength, and elasticity will be promoted at the sacrifice of some ductility (III, Fig. 1). It will be explained in another lesson that sorbite is generally regarded as one of the transition stages assumed by the metal as it passes from its austenitic condition, stable above the critical range, to its pearlitic condition, stable below that range.

Influence of Maximum Temperature. — The influence of the maximum temperature to which steel is heated before being allowed to cool is well shown in Figures 6 to 9 which should be compared with Figures 2 to 5. They refer to steel containing 0.50 per cent carbon and heated to 800 deg. C., while the structures illustrated in Figures 2 to 5 refer to the same steel but heated to 1000 deg. The constitutents are the same, namely, ferrite and pearlite in the furnace cooled samples, ferrite and sorbite in the air cooled samples, but the higher temperature resulted in the formation of larger particles of pearlite or sorbite, evidently because of the formation above the critical range of larger austenitic grains.

Influence of Time at Maximum Temperature. — Maintaining steel for a long time at a high temperature causes the formation of large austenite grains, which in passing through the range are converted into large pearlite or sorbite grains with rejection of free ferrite in hypo-eutectoid steel and of free cementite in hyper-eutectoid steel. It is also noted that the more prolonged the heating the smaller the amount of the excess constituent (free ferrite or free cementite) separating on rapid (air) cooling through the range. This is shown in Figure 10 in which is depicted the structure of steel containing 0.50 per cent carbon heated to 1150 deg. C. for two hours and air cooled. The very large sorbitic grains should be noted as well as the very small proportion of free ferrite.

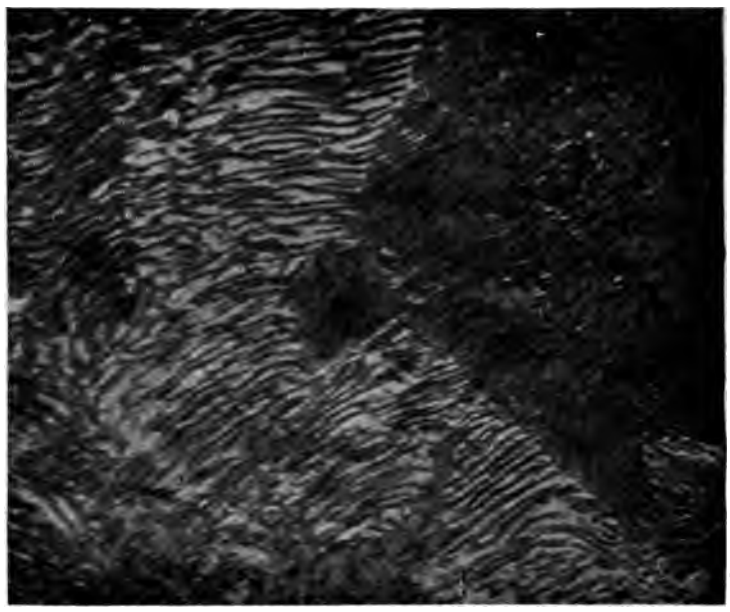
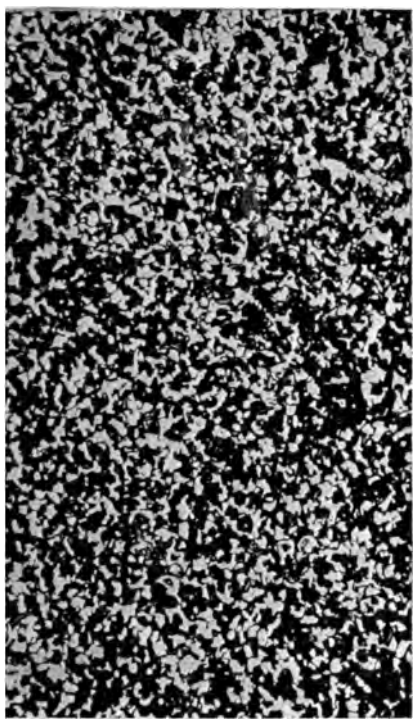


Fig. 5. — Steel. Carbon 1.00 per cent. Magnified 1500 diameters. Pearlite (laminated) passing into sorbite. (Osmond.)

Oil and Water Quenching from Annealing Temperature. — As already explained only steel containing very little carbon may be quenched in oil or water for purposes of annealing, unless, indeed, the double treatment soon to be described be employed when higher carbon steels may be so quenched. The structure of steel containing 0.10 per cent carbon, heated to 950 deg. and quenched in water, is shown in Figure 11, while in Figure 12 is seen the structure of steel containing 0.20 per cent carbon quenched in oil from a temperature of 850 deg. Rapid cooling through the range did not prevent the separation of the bulk of the large amount of excess ferrite present in these steels, hence their softness and ductility even after quenching. They are, however, somewhat stronger and more elastic than similar steels more slowly cooled, (1) because they contain a somewhat smaller proportion of soft free ferrite, (2) because the free ferrite they contain has crystallized into smaller grains, and (3) because their carburized constituent is sorbitic or even martensitic[1] rather than pearlitic.

[1] Martensite is the ordinary constituent of steel hardened by quenching. It is hard and deprived of ductility.



. — Magnified 100 diameters. Heated to
deg. C. and slowly cooled in furnace.

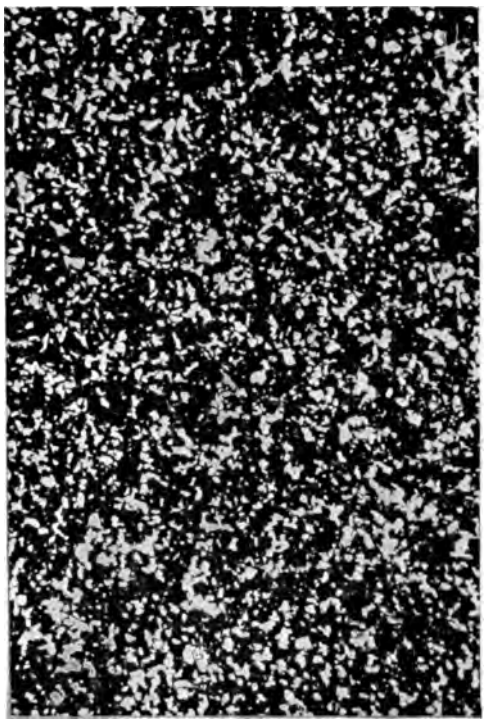
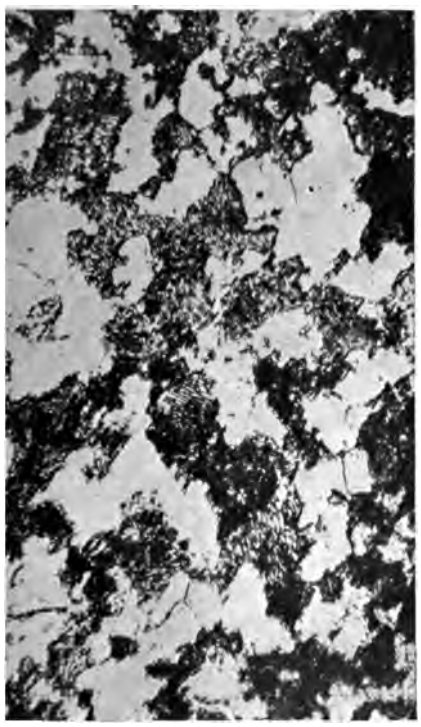


Fig. 8. — Magnified 100 diameters. Heated to 800 deg. C. and cooled in air.



. — Magnified 670 diameters. Heated to
0 deg. C. and slowly cooled in furnace.

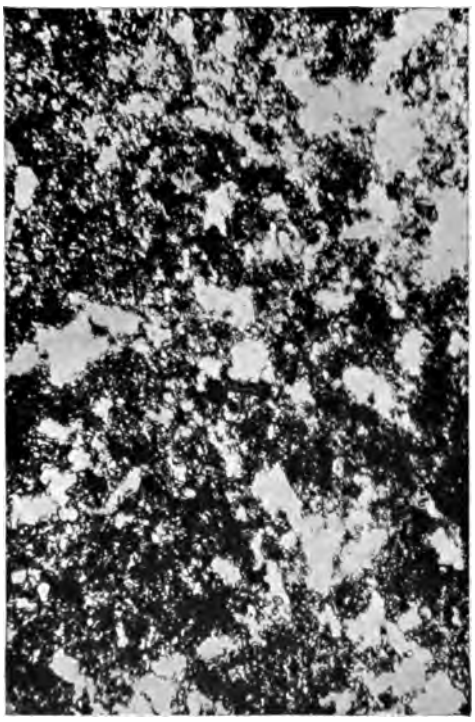


Fig. 9. Magnified 670 diameters. Heated to 800 deg. C. and cooled in air.

s. 6–9. — Steel. Carbon 0.50 per cent. (C. C. Buck, Correspondence Course student.)

Double Annealing Treatment. — It has been stated that the most effective way of retaining in the cold the very fine structure acquired by steel in passing through its critical range consisted in cooling it very rapidly as soon as it emerged from that range, as, for instance, by quenching it in water. This treatment, however, unless the metal contains very little carbon, hardens the steel and deprives it of ductility, whereas annealed steel should not be very hard and should possess much ductility. If this fine grained but hard steel, however, be reheated to a temperature close to but below its critical range, say to from 500 to 650 deg. C., it loses its hardness but retains its fine structure and again becomes ductile (IV, Fig. 1).

The double treatment outlined above fulfils admirably the aims generally sought

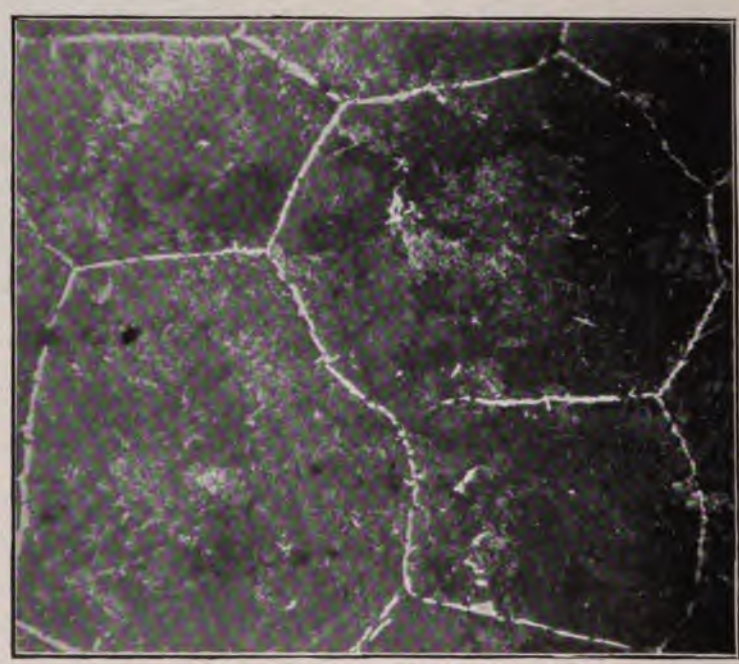


Fig. 10. — Steel. Carbon 0.50 per cent. Magnified 100 diameters. Heated to 1150 deg. C. for two hours and cooled in air. (Boynton.)

in annealing, namely, the production of a very fine structure possessing high strength and elastic limit with fair ductility, in other words toughness and high resistance to wear and to shock. The change of structure taking place on heating hardened steel close to the lower limit of its critical range will be considered at some length in Lesson XIV. It will suffice to note here that the metal passes from a fine martensitic or troostitic condition (the ordinary condition of well-hardened steel) to an equally fine sorbitic condition, possessing in a high degree the physical properties desired. The first heating is sometimes called "grain refining" treatment and the second "toughening" treatment.

The quenching of a piece of steel from above its critical range, while simple enough in the case of very mild steel, presents increasing difficulties as the carbon increases. It should be conducted with care and intelligence and only by experts. Steel con-

taining very little carbon, say not over 0.15 per cent, may be quenched in water, others should be quenched in oil. The Committee on Heat Treatment of the American Society for Testing Materials recommends, in order to lessen the danger of

Fig. 11. — Steel. Carbon 0.10 per cent. Magnified 100 diameters. Heated to 950 deg. C. and quenched in water. (Boylston.)

Fig. 12. — Steel. Carbon 0.20 per cent. Magnified 100 diameters. Heated to 850 deg. C. and quenched in oil. (Boylston.)

cracking, that the object be removed from the oil or water bath before its temperature has fallen below 160 deg. C., or in any event below 100 deg., and that the second treatment be applied within a few hours after the quenching, preferably without ever

allowing the piece to cool below 100 deg. and certainly not below 20 deg. The final properties of the steel will depend upon the temperature of the second heating; the higher that temperature the softer and more ductile will it be, but also the less strong and elastic. For great strength, high elastic limit, and little ductility reheating to 500 deg. should be applied, while for great ductility, at the sacrifice of considerable strength, the reheating should be carried to 700 or 725 deg. For intermediate tensile strength, elastic limit, and ductility such as are desired in the majority of cases, the temperature of the second treatment should be between 600 and 650 deg. C. While from purely theoretical considerations it might be argued that the rate of cooling from this second treatment is immaterial, there is little doubt but that the strength of the steel increases somewhat and its ductility decreases with the rapidity of cooling. This cooling may be performed in the furnace, in air, in oil, or in water.

Fig. 13. — Steel. Carbon 0.50 per cent. Magnified 500 diameters. Heated to 850 deg. C., quenched in water, reheated to 600 deg., and cooled in air. (W. H. Knight in the author's laboratory.)

The double annealing treatment described in the foregoing paragraphs was first suggested by Wallerant of the Creusot Steel Works, France. It was also described by André Le Chatelier and adopted by the French navy. Its use is now general when high physical requirements are to be met.

In Figure 13 is shown the structure of steel, containing some 0.50 per cent carbon, after double annealing. The fineness of the structure should be noted as well as the lack of laminations and the absence of free ferrite. This steel is composed wholly of finely divided sorbite.

Annealing Eutectoid Steel. — While the mechanism of the structural changes taking place on annealing steel has been made clear in the preceding pages, it may not be without interest to consider further and in succession the annealing of eutectoid, hypo-eutectoid, and hyper-eutectoid steel, as these three types of steels have different structures and their annealing involves different structural changes.

Slowly cooled eutectoid steel is composed wholly of pearlite which, upon being heated through the single critical point of the metal, namely $Ac_{3.2.1}$, is converted into a solid solution (austenite). The grains of this austenite are very fine as the steel emerges from its range and they are kept from growing by preventing the steel from reaching a higher temperature. On cooling through $Ar_{3.2.1}$ the metal again becomes pearlitic if it be given time, as, for instance, in cooling in the furnace, while it becomes sorbitic if cooled more quickly, as, for instance, in air in the case of small objects. Should the steel be quenched in water or oil from the annealing temperature and then reheated near but below the point $Ac_{3.2.1}$, the finely martenso-troostitic structure produced by quenching from above the range is converted into very fine sorbite.

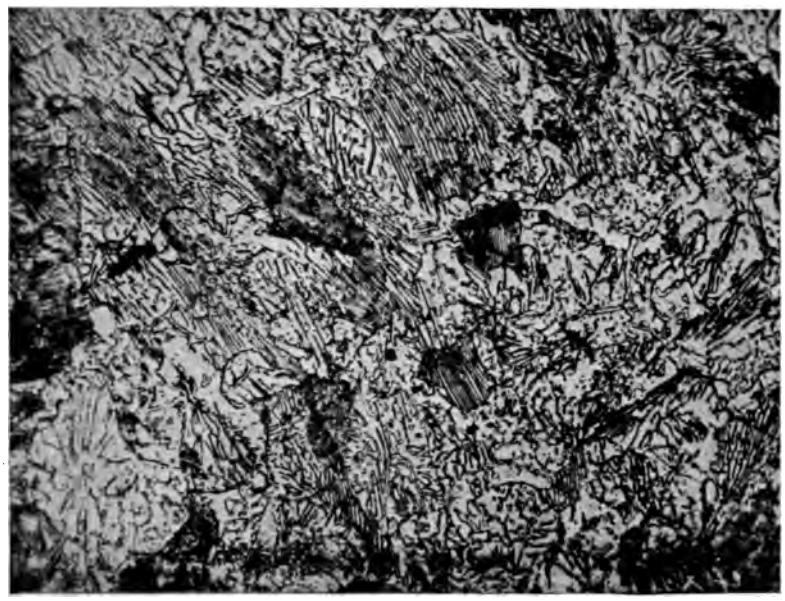


Fig. 14. — Steel. Eutectoid. Magnified 412 diameters. Heated to 800 deg. C. and slowly cooled in furnace. (C. C. Buck, Correspondence Course student.)

It has been explained in Lesson X that, for like treatments, the structure of eutectoid steel is finer than that of either hypo-eutectoid or hyper-eutectoid steel and this holds true in the case of annealed samples, although the difference may not be noticeable when comparing the structure of eutectoid steel with that of hyper-eutectoid steel containing but a slight excess of free cementite.

In Figure 14 is shown the structure of eutectoid steel heated to 800 deg. C. and slowly cooled in the furnace. It is made up of well-developed pearlite. The structure of the same steel, quenched in oil at 825 deg., reheated to 650 deg., and cooled in air, is exhibited in Figure 15. The metal is now composed of fine grained sorbite.

Annealing Hypo-Eutectoid Steel. — Slowly cooled hypo-eutectoid steel is an aggregate of pearlite and free ferrite. On being heated through its critical range, as soon as the point Ac_1 is reached, the pearlite is bodily converted into austenite, while the ferrite still remains free. On further heating, however, it begins to be absorbed by austenite, its absorption being completed as the metal emerges from its Ac_3 point.

Above Ac_3 the steel is composed wholly of homogeneous austenite. On cooling through the critical range, unless, indeed, the cooling be very rapid and sufficient carbon be present, ferrite is again liberated in amount proportional to the slowness of the cooling up to the maximum quantity consistent with the carbon content in the steel. If the cooling be very slow then, for instance in the furnace, the totality of the excess ferrite will be rejected and the residual austenite converted into well-defined pearlite (Figs. 3 and 7), while if the cooling be more rapid, for instance in air in the case of small objects or in oil with larger ones, a portion only of the excess ferrite is liberated while the residual austenite is converted into sorbite (Figs. 4 and 9). The liberation of ferrite taking place during the slow cooling of hypo-eutectoid steel coarsens its structure and is the chief reason why annealed hypo-eutectoid steel

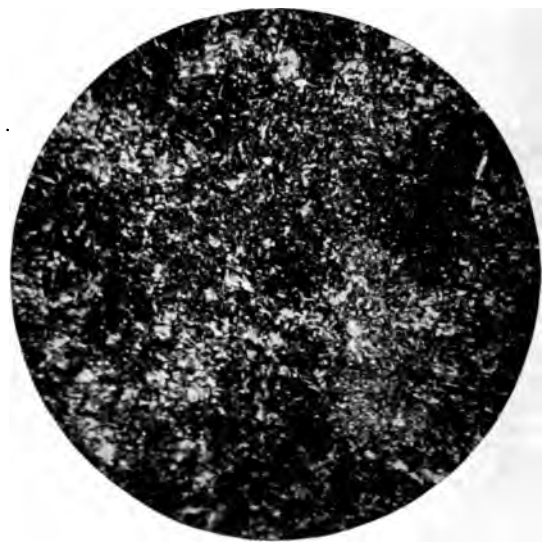


Fig. 15. — Steel. Eutectoid. Magnified 720 diameters. Heated to 825 deg. C., quenched in oil, reheated to 650 deg., and cooled in air. (Boylston.)

cannot have as fine a structure as annealed eutectoid steel. Howe further contends that as hypo-eutectoid steel is heated from Ac_1 to Ac_3 a new crystalline growth takes place which is the coarser the greater the distance between A_1 and A_3, that is, the less carbon in the steel, so that by the time the old structure has been obliterated, i.e. at Ac_3, a new grain has formed which is an additional reason why the structure of hypo-eutectoid steel cannot be refined to the same extent as that of eutectoid steel.

The structure of hypo-eutectoid steel after double annealing has been shown in Figure 13. The rapid cooling through the range prevented the liberation of ferrite, while the second treatment produced sorbite, but this sorbite is not as fine grained as that produced in eutectoid steel by similar treatment.

Annealing Hyper-Eutectoid Steel. — Slowly cooled hyper-eutectoid steel is an aggregate of pearlite and free cementite. On heating it through its critical range, i.e. through its $Ac_{3.2.1.}$ and Ac_{cm} points, pearlite is converted into austenite at the lower point and this austenite absorbs the free cementite as the metal is further heated

from $Ac_{3.2.1}$ to Ac_{cm}. At Ac_{cm} the absorption is complete and the metal composed entirely of austenite. On cooling through the range, if time be given, as for instance in cooling in the furnace, the full proportion of free cementite is again liberated and the residual austenite converted at $Ar_{3.2.1}$ into clearly laminated pearlite (Fig. 16). If the cooling be more rapid, as for instance in cooling small pieces in air, a portion only of the free cementite is set free, while the residual austenite is converted into sorbite. This setting free of cementite, like the liberation of ferrite in hypo-eutectoid steel, coarsens the structure. The coarsening influence of free cementite, however, is far from being as marked as that of free ferrite, chiefly because free cementite is generally present in much smaller proportions. Steel containing as much as 1.50

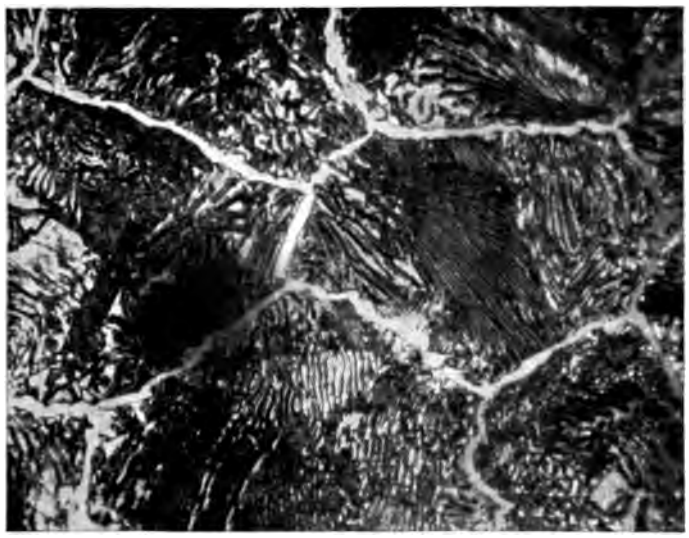


Fig. 16. — Steel. Carbon 1.43 per cent. Magnified 500 diameters. Heated above critical range and slowly cooled in furnace. (Boynton.)

per cent carbon, for instance, contains but 11.50 per cent of coarsening cementite, while steel with 0.40 carbon contains 52 per cent of coarsening ferrite.

In Figure 17 is shown the structure of hyper-eutectoid steel subjected to the double annealing treatment. This treatment prevented the separation of any free cementite and resulted in the production of fine grained sorbite.

Annealing Steel Castings. — It has been mentioned that the very coarse structure of steel castings, called "ingotism" by Howe, was not as readily refined as the structure of steel forgings, its satisfactory annealing often necessitating heating to temperatures considerably higher than the critical range. Notwithstanding their greater resistance to the annealing treatment, successfully annealed castings may possess physical properties fairly equal to those of forgings. In Figure 18 is shown the structure of cast steel containing some 0.30 per cent of carbon and properly annealed. The presence of a relatively small amount of free ferrite will be noted. When highly magnified the carbon-holding constituent should have a sorbito-pearlitic appearance.

Spheroidizing of Pearlite-Cementite. — On slow cooling through the critical range, austenite of eutectoid composition is converted into pearlite made up of distinct

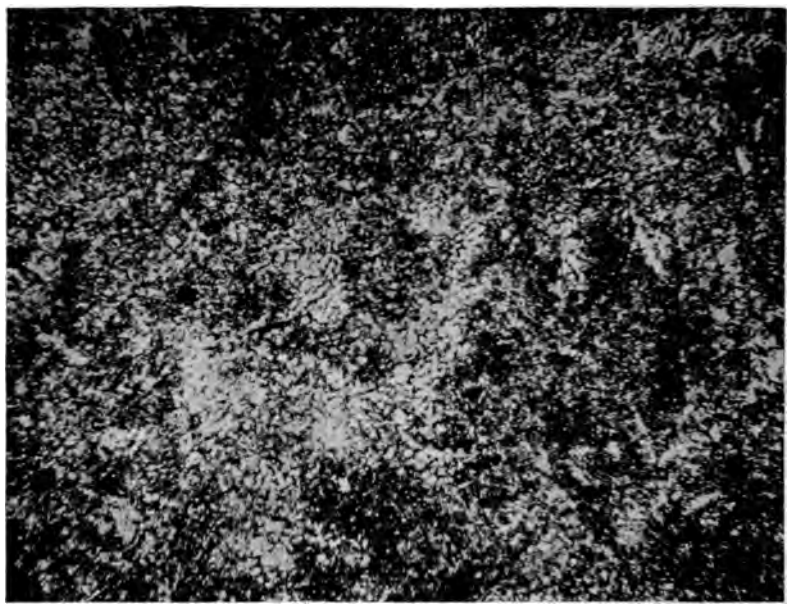


Fig. 17. — Steel. Carbon 1.25 per cent. Magnified 670 diameters. Heated to 800 deg. C. and quenched in oil, reheated to 600 deg. and air cooled. (C. C. Buck, Correspondence Course student.)

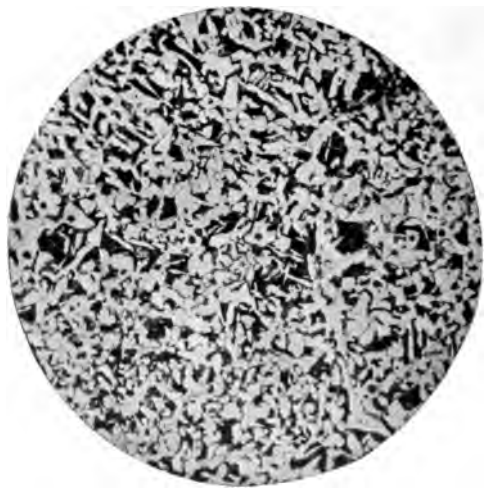


Fig. 18. — Steel. Cast. Carbon 0.30 per cent. Magnified 100 diameters. Annealed. (W. J. Burger, Correspondence Course student.)

parallel plates or lamellæ alternately of ferrite and cementite. This condition of the cementite of pearlite, however, is not final, it is not structurally stable, if it can be thus expressed, for if the steel be kept for a sufficiently long time at a temperature

but slightly below the range, preferably between 600 and 700 deg. C., the cementite shows a marked tendency to form rounded particles or, as it has been well said, to "spheroidize." This phenomenon is shown in Figure 19 in the case of 1.24 per cent carbon steel. The cementite now occurs as small irregular grains embedded in ferrite. This variety of pearlite, if we can still speak of it as pearlite, is sometimes called "granular" pearlite. Some writers state that the essential factor in this spheroidizing process is extremely slow cooling between 700 and 600 deg. Since the point Ar_1 generally occurs a little below 700 deg. it may well be asked whether (1) the spheroidizing of pearlite is due to excessively slow cooling through that point or whether (2) lamellar pearlite must first be formed by moderately slow cooling through Ar_1, being afterwards converted into spheroidized pearlite below Ar_1. The evidences at hand are not conclusive. Spheroidized pearlite is softer, less tenacious, and more ductile than lamellar pearlite. The author has heard of this

Fig. 19. — Steel. Carbon 1.24 per cent. Magnified 1000 diameters. Spheroidized cementite. (Osmond.)

spheroidizing treatment having been applied to high carbon steel in order to soften it so as to facilitate its machining, it being afterwards reheated above its range and made pearlitic, sorbitic, or martensitic according to requirements.

Varieties of Pearlite. — From the foregoing it will be evident that several varieties of pearlite are to be considered and that the physical properties of steel will depend greatly upon the character of the pearlite it contains. Arnold considers four varieties of pearlite which are well illustrated in Figure 20. His first phase, which he calls "sorbitic" pearlite, is generally called sorbite by other writers. The character and physical properties of sorbite have been described, as well as some of the conditions necessary to its formation. His second and third phases, to which he gives the names respectively of "normal" and "laminated" pearlite, are both true pearlite, the thicker lamellæ of the latter being due to a slower cooling through the critical range. His fourth phase is pearlite in the process of spheroidizing.

Graphitizing of Cementite. — It will be explained in another lesson that the carbide Fe_3C (cementite) is not the most stable form that can be assumed by carbon

Showing the Properties of Pearlite and its Decomposition Product. Fe_3C represented Black.

Mechanical Properties of Mass.	Microstructure.	Segregation Stages.
Maximum tensile stress about 70 tons per square inch. Elongation on 2 inches = about 10 per cent.		1ST PHASE. "Sorbitic" Pearlite with emulsified Fe_3C. Very dark on etching.
Maximum tensile stress about 55 tons per square inch.. Elongation on 2 inches = about 15 per cent.		2ND PHASE. Normal pearlite with semi-segregated Fe_3C. Dark on etching.
Maximum tensile stress about 35 tons per square inch. Elongation on 2 inches = about 5 per cent.		3RD PHASE. Laminated pearlite with completely segregated Fe_3C. Exhibiting a play of gorgeous colours when lightly etched.
Maximum tensile stress about 30 tons per square inch.		4TH PHASE. Laminated pearlite passing into massive Fe_3C and ferrite.

NOTE.—It is important to remember that in a single section of steel two or even all three phases of pearlite may be observed in juxtaposition gradually merging into each other.

Fig. 20. — (Arnold).

when alloyed with iron. It will be shown that cementite tends to break up into iron and graphite according to the reaction

$$\underset{\text{cementite}}{Fe_3C} = \underset{\text{ferrite}}{3Fe} + \underset{\text{graphite}}{C}$$

and that the graphite form is the final stable condition of carbon. This graphitizing tendency of cementite remains latent unless the conditions be favorable to its activity. These conditions are (1) long exposure to a temperature exceeding the critical range and slow cooling,[1] (2) the presence of much carbon, and (3) the presence of silicon or of some other elements exerting a similar influence. It will be shown that this tendency of cementite to be converted into graphite and iron is responsible for the production of so-called malleable castings and, probably, also for the production of gray cast iron. In the case of steel, because of the relatively small amount of carbon present (not exceeding 1.75 or at the most 2 per cent), the graphitizing tendency is slight. Long exposure of hyper-eutectoid steel, especially if it contains more than one per cent carbon, however, to a temperature exceeding its critical range, is always likely to produce a small amount at least of graphitic carbon greatly impairing thereby, if not ruining, the metal. An instance of graphite formation in high carbon steel is shown in Figures 21 and 22. There is little doubt but the free cementite present in hyper-eutectoid steel, and formed as the steel cools from its Ar_{cm} to its $Ar_{3.2.1.}$ point, is more readily converted into graphite than the cementite included in the pearlite. Once the graphitizing is started, however, it may be carried to completion and include the whole of the cementite present. This indeed is what happens in certain grades of malleable cast iron and of gray cast iron which contain practically the totality of their carbon in the form of graphite. The presence of some free cementite appears to be necessary to start the graphitizing, which would explain why it does not take place in hypo-eutectoid steel. The author at least never had a case of graphite formation in such steels brought to his attention nor was he ever able to produce graphite in hypo-eutectoid steel.

Burnt Steel. — When high carbon steel is heated to a temperature approaching its melting-point, it becomes extremely red short as well as cold short, its fracture becomes very coarse and shiny and these defects cannot be cured short of remelting the metal. The steel in such condition is said to be burnt. These results are apparently brought about by the evolution of gases under the influence of a high temperature, chiefly carbon monoxide, resulting from atmospheric oxygen finding its way through the pores of the metal and combining with some of the carbon, although according to Howe other occluded gases, such as hydrogen and nitrogen, may also contribute. These gases force the crystalline grains apart, destroying their cohesion, hence the brittleness of the metal. Oxidized membranes are also frequently found surrounding some of the grains, their presence readily explaining the impossibility of restoring burnt steel by forging since they would prevent the welding of adjacent grains. Instances of the structure of burnt steel are shown in Figures 23 and 24. Howe defines burning as being "a mechanical separation of the grains on extreme overheating." Some writers have argued, apparently on good ground, that burning will not take place unless the steel has been heated to so high a temperature that it has actually begun to melt, the explanation being perfectly consistent with the well-known

[1] One or two instances have been cited of graphite having been formed below the critical range.

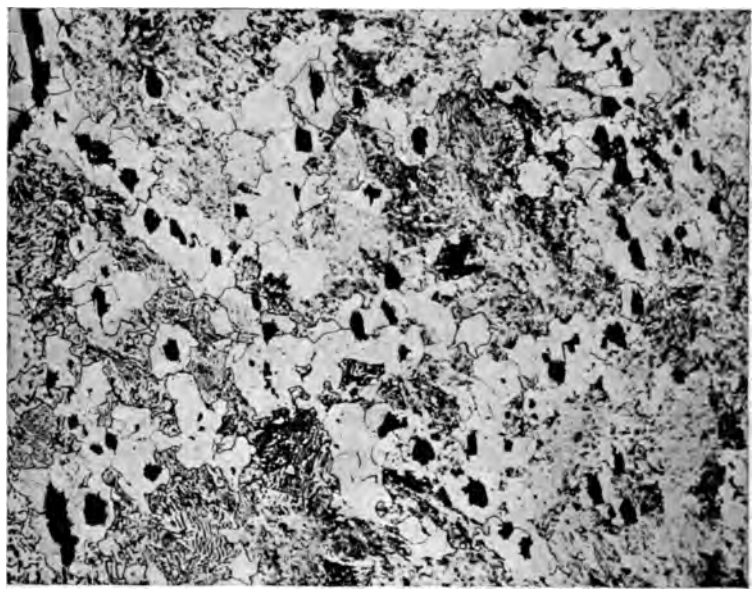


Fig. 21. — Steel. Carbon 1.25 per cent. Magnified 150 diameters. Annealed five hours at 830 deg. C. (C. C. Buck, Correspondence Course student.)

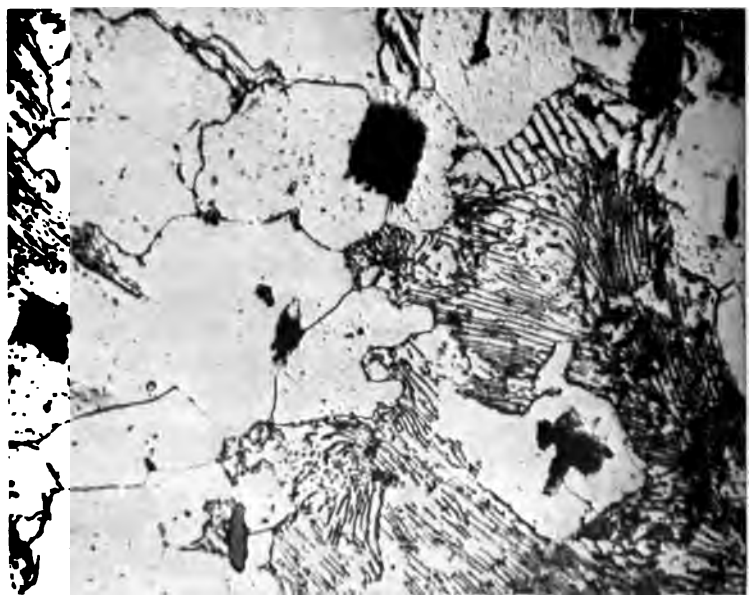


Fig. 22. — Steel. Carbon 1.25 per cent. Magnified 670 diameters. Annealed five hours at 830 deg. C. (C. C. Buck, Correspondence Course student.)

act that high carbon steel burns much more readily than low carbon steel. To make he matter clear let us consider the diagram of Figure 25 in which the solidification eriod of steel is shown as influenced by its carbon content. This diagram will be liscussed at greater length in another lesson. Let us for the present note (1) that s the carbon increases from 0 to 2.0 per cent the solidification of the steel is lowered rom *A* to *B*, that is from 1500 deg. C. to 1325 deg., (2) that while carbonless iron olidifies at a constant temperature, namely 1500 deg., as the carbon increases, the ange of temperature covered by the solidification period increases likewise, extending from *B* to *C* with 2 per cent carbon, that is from 1325 to 1130 deg. *C*. *ABC* then epresents the solidification zone of steels of increasing carbon content and the eating of the metal to any point within this zone, when it is partly melted, will ause it to burn. It follows from this that carbonless iron and very low carbon steel

Fig. 23. — Burnt steel. Carbon 1.24 per cent. Magnified 20 diameters. Quenched at a white heat. Unetched. (Osmond.)

Fig. 24. — Burnt steel. Magnified 30 diameters. (Stead.)

an be heated to a very high temperature without burning, while the danger of burning increases with the carbon. With 0.50 per cent carbon, for instance, the burning one extends from 1400 to 1450 deg., with 1.0 per cent it extends from 1310 to 1400 leg., with 1.50 per cent carbon from 1210 to 1360 deg. In short, as the carbon increases the steel burns more readily (1) because its melting-point is lowered and (2) ecause its solidification zone, which is also its burning zone, is widened. According o the theory it should not be possible to burn carbonless iron, and indeed the author loes not know that the claim has ever been made that carbonless iron could be burnt.

If *ABC* represents a burning zone into which steel cannot be brought without aving its useful qualities destroyed, we naturally ask why all steels are not so injured eeing that they must pass at least once through this zone in cooling from the molten ondition. The reason why steel does not burn on solidifying and further cooling is xplained by Howe on the ground that while steel ingots or other castings solidify, nuch hydrogen is given out which may mechanically restrain the oxygen from entering and also counteract it, preventing thereby the evolution of CO from within and he formation of oxidized films, the chief causes of burning. It is also possible, Howe ays, that the greater kneading which an ingot undergoes cures burning, while the

slight kneading possible in reworking a steel bar does not. This, however, would not explain why steel castings, which undergo no work at all, are not burnt, unless it is because they are generally protected from atmospheric oxidation by their molds (Howe).

Burning should not be confounded with overheating. Overheated steel has a very coarse structure and fracture, but it can be restored by heat treatment alone, or at least by heating and forging, while burnt steel is incurable. Overheating results from heating close to but below AC (Fig. 25), generally for a considerable length of time, while, as explained, the temperature in burning is carried above AC.

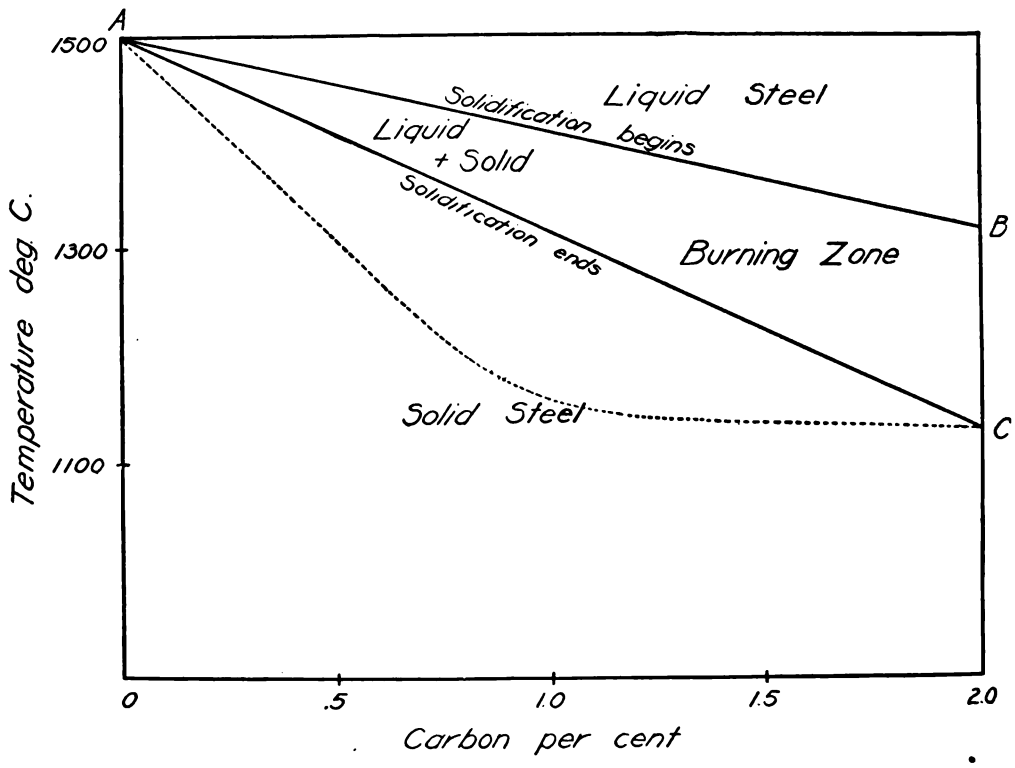


Fig. 25. — Diagram depicting the burning temperature range.

Important results recently obtained by Gutowsky would place the end of the solidification of various carbon steels as indicated by the dotted line in Figure 25. If these are the correct temperatures at which solidification is complete, it follows that the burning zone is wider than was generally believed before the publication of these results.

Crystalline Growth of Austenite Above the Critical Range. — Above its critical range steel is composed of polyhedric crystalline grains of austenite, which are made up of small crystals (probably octahedra) similarly oriented in the same grain but whose orientation changes from one grain to the next. Indeed it is this lack of uniformity of the orientation of the crystalline matter building up the grains that gives existence to these grains, for if all the small crystals of which they are composed were similarly oriented, clearly there would be but a single allotrimorphic crystal or grain.

If steel be maintained for a long time above its critical range, the austenite grains of which it is composed show a tendency to grow in size through adjoining grains assuming like crystalline orientation and, therefore, merging into a single and correspondingly larger grain. This growth increases with the temperature and with the duration of the treatment. Given a sufficiently long time and sufficiently high temperature, but one grain must be formed. This, as already seen in Lesson X, is actually what takes place in meteorites during the cooling of which the prevailing conditions are such as to produce this uniformity of orientation. It follows from the above considerations that on annealing, if the metal be kept a long time above its critical range, even but slightly above it, a coarser austenite will be formed which in turn implies, after slow cooling, a coarser pearlitic or sorbitic structure. In hypo-eutectoid steel the grains of austenite will expel some free ferrite, and in hyper-eutectoid steel some free cementite, before being converted into pearlite, but the final pearlite grains will nevertheless increase in size with the size of the original austenite grains. The structure of steel containing 0.50 per cent carbon kept two hours at 1150 deg. C. and cooled in air has been shown in Figure 10. The very large sorbitic grains formed prove the existence above the range of equally large, or even larger, austenitic grains. The cooling through the range was so rapid that but a small amount of free ferrite was separated, the sorbite grains, therefore, representing nearly the exact size of the austenite grains.

In Figure 26 an attempt has been made to depict this relation between the austenitic structure above the range and the corresponding pearlitic or sorbitic structure below the range. The steel considered is supposed to be hypo-eutectoid and to contain, after slow cooling, a large proportion of free ferrite. *A* is intended to represent a piece of this steel made up of nine relatively small austenitic grains formed on short exposure above the range. On cooling through the range ferrite is liberated and the residual austenite grains converted into as many pearlite grains as shown in *A'*. The small squares of the matrix surrounding the pearlite grains represent as many small ferrite grains. After a longer exposure, possibly at a higher temperature, the steel will be made up of larger austenite grains, say of four grains as shown in *B*, and these, on slow cooling through the range, will be converted after rejection of ferrite into four pearlite grains as indicated in *B'*. Theoretically, at least, we may assume that the temperature above the range may be so high and the exposure at that temperature so long that but a single austenite grain is formed, the entire mass having assumed a uniform crystalline orientation as shown in *C*. On slow cooling a single pearlite grain would then be formed surrounded by free ferrite in the form of small grains as depicted in *C'*. An exceedingly slow cooling through and below the range would have a tendency to cause the free ferrite to crystallize into larger grains and eventually to form but a single grain as indicated in *C''*.[1] Finally, as will be later explained, on very long exposure to a high temperature the cementite should, theoretically at least, be converted into as many graphite particles as there are austenite grains and, therefore, into a single graphite particle in case there is but a single grain of austenite, the steel then consisting, after slow cooling, of a kernel of graphite surrounded by uniformly oriented ferrite as shown in *C'''*. As already explained, however, this breaking up of cementite into graphite and ferrite does not take place unless a considerable amount of carbon is present, namely over 1 per cent.

[1] Such slow cooling, as previously explained, would also have a tendency to cause the spheroidizing of cementite.

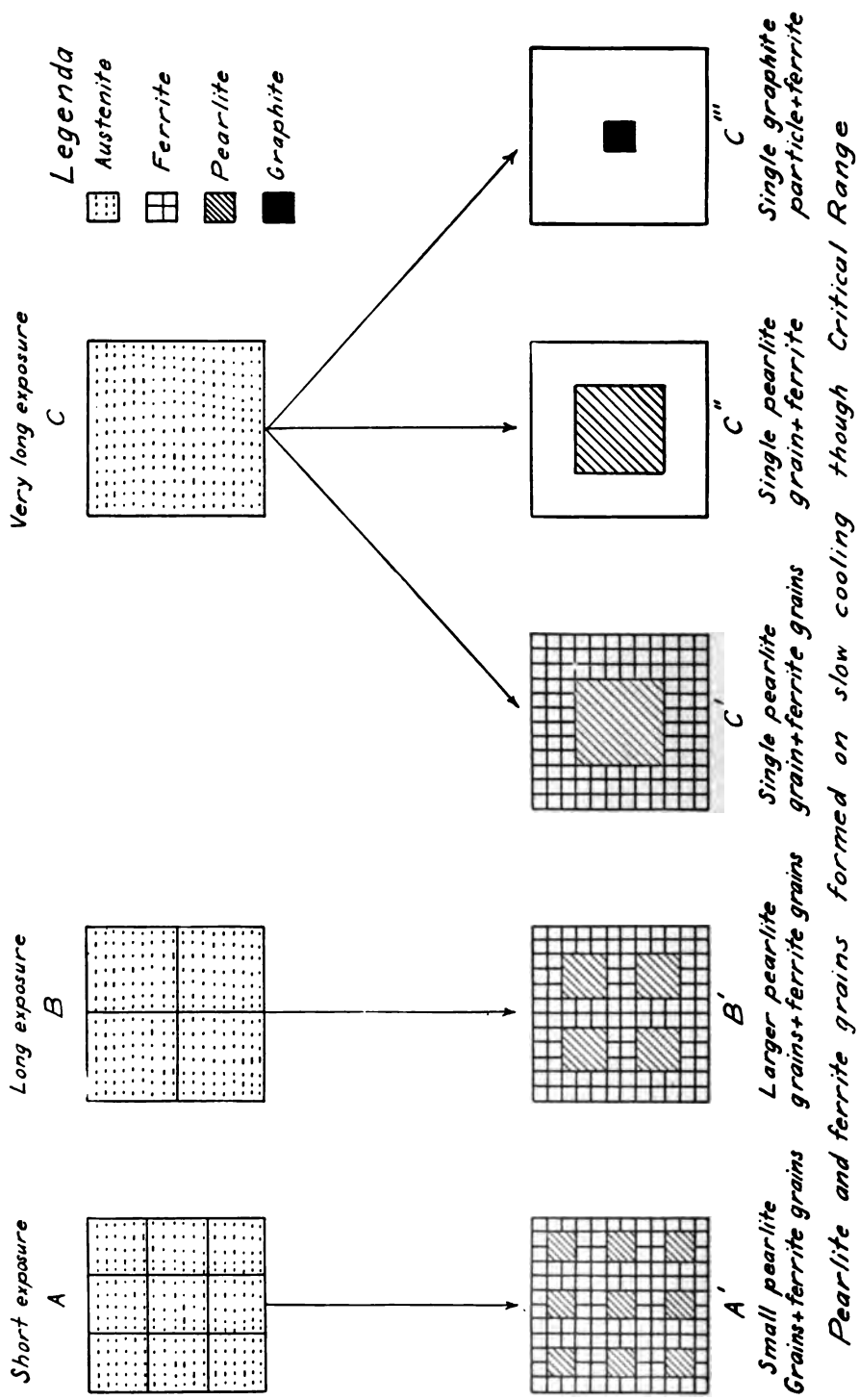

Austenite grains formed above Critical Range
Short exposure
A
Long exposure
B
Very long exposure
C
Legenda
Austenite
Ferrite
Pearlite
Graphite
Small pearlite
Grains+ferrite grains
A'
Larger pearlite
grains+ferrite grains
B'
Single pearlite
grain+ferrite grains
C'
Single pearlite
grain+ferrite
C"
Single graphite
particle+ferrite
C"'
Pearlite and ferrite grains formed on slow cooling though Critical Range

Fig. 20.

The conditions depicted in A', B', C', C'', and C''' are conditions of equilibrium, according to the phase rule, since but two phases are present. It is now believed, however, that A', B', C', and C'' represent metastable equilibrium while D, only, represents stable equilibrium. The phase rule will be considered in another lesson when these remarks will be made clear.

Crystalline Growth of Ferrite Below the Critical Range. — Stead in 1898 showed that *strained* ferrite, when heated close to but below the critical range of the metal, undergoes a marked crystalline growth caused by adjoining ferrite grains assuming the same crystalline orientation and therefore merging into a larger grain. It seemed evident from Stead's experiments that unless the ferrite be strained (through cold working or otherwise) it will not grow on annealing, and also that the presence of a relatively small amount of carbon (some 0.15 per cent or more) effectively prevents the growth of the ferrite grains, apparently because of the pearlite particles standing

Fig. 27. — Steel. Carbon 0.05 per cent. Magnified 6 diameters. Subjected to Brinell ball test under pressure of 6000 kilograms and heated to 650 deg. C. for seven hours. Vertical section through bottom of spherical depression. (J. O. Connolly in the author's laboratory.)

in their way and preventing their merging. The author recently conducted in his laboratory some experiments, the results of which throw additional light upon this crystalline growth.[1]

The following extracts from a paper by the author to be presented at the sixth Congress of the International Association for Testing Materials describe briefly some of the most significant results obtained.

In Figure 27 is shown the slightly magnified structure of a steel containing 0.05 per cent carbon which had been subjected to the Brinell ball test [2] under a pressure of 6000 kilograms and then annealed at 650 deg. C. for seven hours. The section shown is a vertical one passing through the bottom of the spherical depression made by the

[1] These experiments were made by J. O. Connolly, at the time a research student at Harvard University, now with the American Steel and Wire Co.

[2] In using the Brinell ball test as a suitable means of straining ferrite in order to study its growth on annealing the author followed Charpy.

10mm. ball used. It will be obvious that the strain was most severe at *A*, that is at the very bottom of the depression, and that it decreased gradually in intensity from *A* to *D*. The following features of the structure should be noted as having special significance: (1) At *D* where the metal was but slightly if at all strained no crystalline growth occurred, (2) at *C* where the strain must have been more severe a sudden growth of maximum intensity has taken place, (3) from *C* to *B* as the severity of the strain increases the crystalline growth shows a gradual *decrease*, and (4) from *B* to *A*, that is, with further increase of the intensity of the strain, no crystalline growth has taken place. These observations point to the conclusion that ferrite grains will not grow on annealing below the critical range unless they have been subjected to a certain stress creating a certain strain, and that they will not grow if

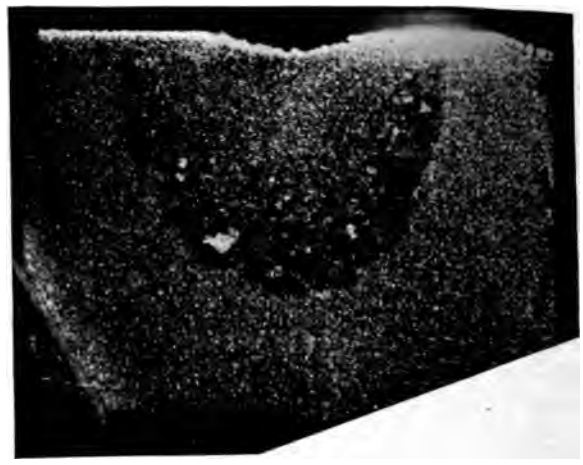


Fig. 28. — Steel. Carbon 0.05 per cent. Magnified 6 diameters. Subjected to Brinell ball test under pressure of 3000 kilograms and heated to 650 deg. C. for seven hours. Vertical section through bottom of spherical depression. (J. O. Connolly in the author's laboratory.)

that stress, and therefore the resulting strain, has been exceeded. In other words, they point to the existence of a critical strain producing growth, strains of greater or less magnitude being ineffective. The narrow region occupied by the critically strained metal should also be noted as well as the very sharp line of demarcation between the critically strained and the under-strained metal. The separation of the critically strained metal from the over-strained is not so sharp.

Similar experiments were repeated many times and like results always obtained.

A piece of the same steel was subjected to exactly the same treatment, except that the ball pressure applied was 3000 kilograms or half the pressure applied to the previous one. The crystalline growth resulting from the annealing of this sample is shown in Figure 28. Because of the smaller stress applied, the critically strained portion of the metal is nearer the depression. This would naturally be expected. Here, as in the previous case, we have three distinct regions: (1) the metal surrounding the depression and extending to a certain distance which was too severely strained to

grow, (2) the critically strained metal in the form of a spherical shell, and (3) the rest of the metal unstrained or too feebly strained for the growth to take place. Figure 29 is a section through a similar sample, the specimen having been ground level with the bottom of the depression. The occurrence in this section of a ring showing crystalline growth will be readily understood.

In Figure 30 is shown the structure of a bar of the same steel which after having been completely bent was subjected to annealing (seven hours at 650 deg. C.). A piece of the bent portion of this bar was then cut and a longitudinal section through its center prepared for microscopical examination. It will be obvious that the upper part of the bent portion of the bar was subjected to severe tension and the under part to severe compression. Somewhere between the upper and lower parts a

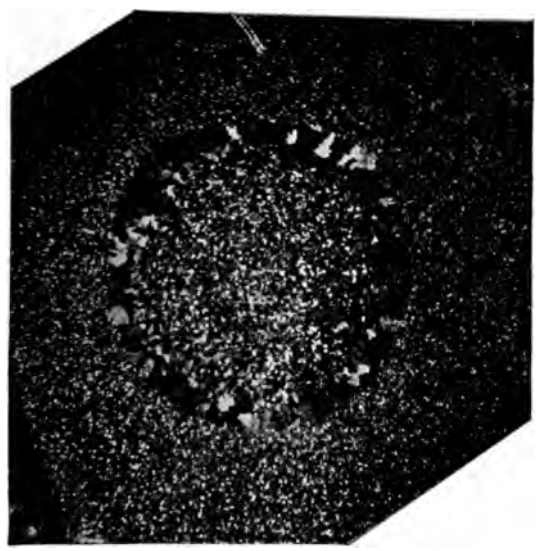


Fig. 29. — Steel. Carbon 0.05 per cent. Magnified 6 diameters. Subjected to Brinell ball test under pressure of 3000 kilograms and heated to 650 deg. C. for seven hours. Horizontal section through bottom of spherical depression. (J. O. Connolly in the author's laboratory.)

neutral plane existed which was subjected neither to tension nor to compression, and in the vicinity of this plane the metal was but slightly strained. Moving in both directions from this neutral plane, the metal becomes gradually more severely strained. Figure 30 shows that (1) in the center of the bar no growth took place, the metal being here under-strained, (2) as soon as the critically strained portion was reached a very abrupt growth occurred of maximum intensity, and (3) this growth decreased gradually as the metal became more severely strained, being very slight if existing at all where the strain was maximum, that is, near the upper and under parts of the bend. The widening of the central zone, free from growth as the distance from the bend increases, is also consistent with the existence of a critical strain for it is evident that the portion of unstrained or under-strained metal increases with that distance. Incidentally this experiment shows that tension is apparently as effective as com-

pression in producing crystalline growth, there being apparently no difference in the size of the ferrite grains between the upper and under parts of the bar. The critically strained portions occupy also nearly the same position with regard to the outside surfaces, that is, they occur at the same depth. Their width also appears to be the same.

Bars of the same steel were subjected to compression, shearing, and twisting stresses and the results obtained were in every case consistent with the existence of a critical strain.

With a view of securing some data in regard to the magnitude of the critical stress needed to induce growth on annealing, a number of bars of the same steel were subjected to tensile stresses of increasing intensity, annealed at 650 deg. seven hours, and in every case a cross section of the strained and annealed bar was prepared for micro-

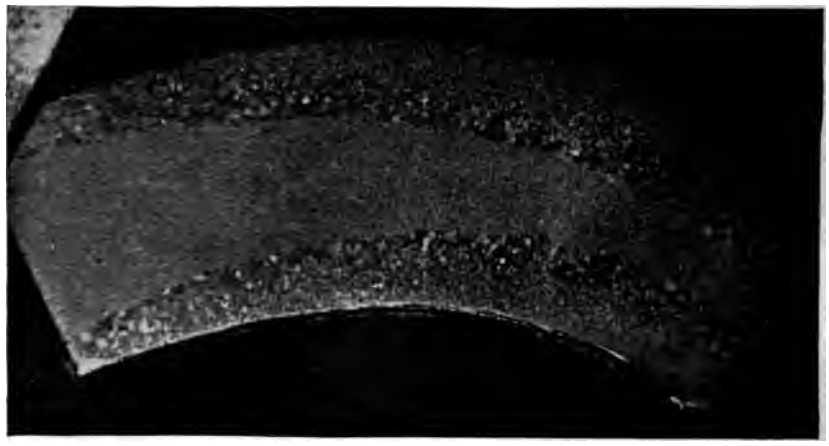


Fig. 30. — Steel. Carbon 0.05 per cent. Magnified 3 diameters. Bar bent double and heated to 650 deg. C. for seven hours. Longitudinal section through center of bent portion. (J. O. Connolly in the author's laboratory.)

scopical examination. The elastic limit or rather yield point of the metal was in the vicinity of 28,000 lbs. per square inch, and its ultimate strength 45,600 lbs. per square inch.

In Figures 31, 32, 33, and 34 are shown the structures of the bars subjected respectively to stresses of 38,000, 40,000, 42,000, and 44,000 lbs. per square inch.

These tensile tests afford another conclusive evidence of the existence of a critical strain and the fact that a stress of 40,000 lbs. per square inch produces a marked growth while stresses but slightly inferior or superior, namely, 38,000 and 42,000 lbs. per square inch do not induce growth is an indication of the narrowness of the range of the critical stress.

Brittleness of Low Carbon Steel. — The crystalline growths and other structural changes described in the foregoing pages lead naturally to the consideration of the brittleness occasionally exhibited by low carbon steel. Since steel containing very little carbon is essentially made up of ferrite, its occasional brittleness must be due to the occasional brittleness of ferrite, a constituent by nature soft and ductile. Stead has indicated two kinds of brittleness from which ferrite may, and occasionally does,

suffer, namely, (1) "inter-granular" brittleness and (2) "inter-crystalline" or "cleavage" brittleness.

By inter-granular brittleness is meant a lack of cohesion between the ferrite grains leading to ready fracture under shock, the line of fracture following the boundary

Fig. 31. — Tensile stress, 38,000 lbs. per sq. in.

Fig. 33. — Tensile stress, 42,000 lbs. per sq. in.

Fig. 32. — Tensile stress, 40,000 lbs. per sq. in.

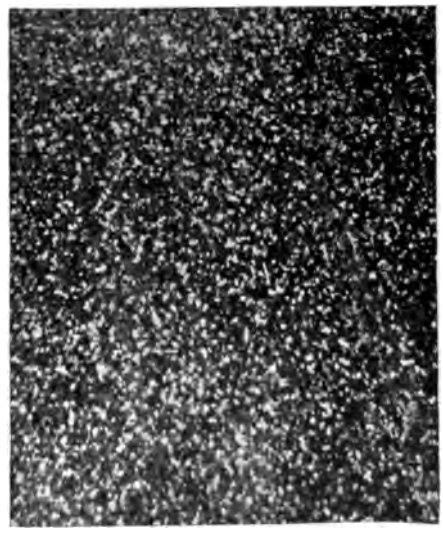


Fig. 34. — Tensile stress, 44,000 lbs. per sq. in.

Steel. Carbon 0.05 per cent. Magnified 6 diameters. Strained by tension and heated to 650 deg. C. for seven hours. Cross sections of strained bars. (J. O. Connolly in the author's laboratory.)

lines of the grains. Such brittleness is usually due to the presence of impurities forming brittle and more or less continuous membranes surrounding the grains. The presence of much phosphorus, however, appears to produce inter-granular brittleness without producing surrounding membranes.

Inter-crystalline or cleavage brittleness is caused by the ferrite grains assuming *nearly* the same crystalline orientation so that the plane of fracture follows the cleavage planes and passes from grain to grain almost in a straight line. The diagram shown in Figure 35 will make this clear. The cross lines represent the cleavage planes in each grain. In *B* the metal is made up of large ferrite grains but the crystalline orientation of these grains is so heterogeneous that a line of fracture cannot readily be developed and pass from grain to grain, the abrupt change of crystalline orientation encountered at each boundary line acting as an effective obstruction to its advance. In *A*, on the contrary, while the grains are smaller they have nearly the same orientation, hence fracture may proceed from grain to grain with much greater ease and in a nearly straight line. Fortunately, so uniform a crystalline orientation

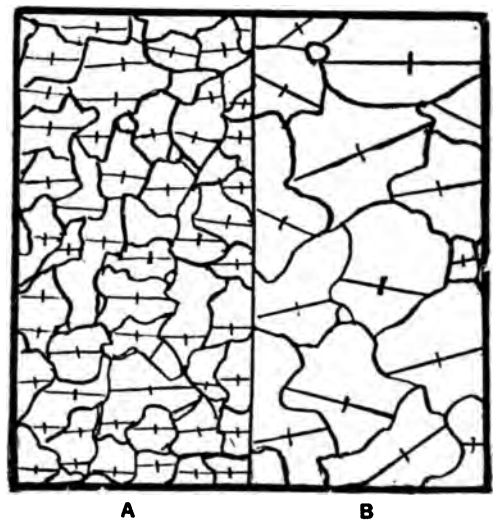


Fig. 35. — (Stead.)

is not often met with and cleavage brittleness is a rather rare occurrence. It can be cured by reheating the steel to 900 deg. or higher.

Stead also noticed that low carbon steel plates rolled below the critical range and, therefore, strained, and annealed likewise below the range, often exhibit a tendency to break in three directions, namely, at 45 deg. to the direction of rolling and at right angles with the surface of the plates, that is, in the directions of the three cleavage planes of a cube having four faces at 45 deg. to the edges, and two faces parallel to the surface of the plates. This he calls "rectangular" brittleness. "We are led from this to conclude," Stead writes, "that, just as light impresses a latent image on a bromide photographic plate which cannot be seen but is developed and made manifest by the action of certain chemical agencies, so the rolling appears to impress a latent disposition in the steel to crystallize in certain fixed positions, and annealing develops it afterwards." The brittleness here referred to is undoubtedly caused by the crystalline growth of strained ferrite when annealed below its critical range as fully explained in this lesson, the formation of large ferrite grains naturally causing brittleness. This kind of brittleness is sometimes called "Stead's brittleness." No very satisfactory explanation has so far been offered to account for this greater brit-

tleness in certain directions. It may be that the large crystalline grains of ferrite produced have nearly the same orientation and that they are so oriented as to lead to easy inter-crystalline rupture in the directions indicated.

Experiments

The student should procure samples of hypo- and hyper-eutectoid steels, cast, hot-worked, and cold worked. These should be microscopically examined and, if possible, photographed. They should then be annealed, following the instructions given in this lesson, and cooled at various rates, to wit, in furnace, in air, and, in the case of low carbon steels, in oil or even in water if the steel does not contain over 0.15 per cent carbon. The structure of each sample should be compared to the structure of the same steel before annealing and the structural changes resulting from the annealing operation carefully noted.

It is advisable to subject at least one sample of hypo-eutectoid steel and one sample of hyper-eutectoid steel to the double annealing treatment, noting the finely sorbitic structure produced by this operation.

Samples of hyper-eutectoid steel, preferably containing not less than 1.25 per cent carbon, should be subjected to (1) spheroidizing treatment and (2) graphitizing treatment, and their structure carefully examined.

A sample of hyper-eutectoid steel should be heated into its burning zone and the resulting structure examined.

A small sample of steel containing not more than 0.10 per cent carbon should be filed very smooth, subjected to the ball test under a pressure of some 3000 kilograms, and annealed to 650 or 700 deg. for at least five hours. A vertical section and an horizontal section passing through the bottom of the spherical depression should be prepared for microscopical examination and the location and magnitude of the crystalline growth noted.

It is desirable that all samples should be photographed, using suitable magnifications.

Examination

I. Assuming a forged steel containing 0.50 per cent carbon, what annealing treatment would you recommend in order to produce: (1) great softness, (2) hardness and great strength but little ductility, and (3) a fair combination of strength, elasticity, and ductility?

II. Assuming a steel containing 0.10 per cent carbon, what treatment would you recommend to produce maximum strength?

III. Assuming a steel containing 1.25 per cent carbon, what treatment would you recommend to produce a desirable combination of strength, elasticity, and ductility so that the metal while tenacious will satisfactorily stand wear and shocks?

IV. Explain how steel can be made sorbitic by annealing.

V. Explain the difference in physical properties between sorbitic and pearlitic steel containing the same amount of carbon.

VI. Explain why the structure and fracture of annealed hypo-eutectoid steel not be made as fine as the structure and fracture of annealed eutectoid

VII. Describe and explain the burning of steel.

VIII. Explain the relation existing between the dimension of austenite grains fc above the critical range and the pearlite grains formed on passing th the range.

LESSON XIII

THE HARDENING OF STEEL

References have already been made in these lessons to the invaluable property possessed by iron, containing a sufficient amount of carbon, of becoming extremely hard when suddenly cooled from a high temperature as, for instance, by quenching in water from a bright red heat. This operation is known as the hardening of steel. The close relation existing between the hardening of steel and its critical range, which has also been alluded to, provides the key to the rationale of the hardening operation. This operation consists of two distinct steps (1) heating to the hardening temperature and (2) cooling from that temperature.

Heating for Hardening. — In order to harden steel it is necessary first to heat it above its critical range, because it is in passing through that range that it acquires hardening power. Any attempt at hardening it by cooling it suddenly from a temperature inferior to its critical range would result in but a very slight, if any, increase of hardness. It is evident, therefore, that to possess hardening power steel must be in the condition of a solid solution since the aggregate of ferrite and cementite formed on slow cooling through the critical range cannot be hardened by sudden cooling. The metal should not be heated much above the top of its range, because in so doing we coarsen its structure as explained in previous lessons, while we do not increase, materially at least, its hardening power, and our aim in hardening should be to secure maximum hardness and finest possible structure. Quenching from a temperature greatly exceeding the critical range, moreover, increases the danger of warping and cracking the objects in the quenching bath. Nor should the steel be heated to a temperature much above its critical range and then cooled to that range before quenching, as sometimes recommended, because its structure is then likewise coarsened by the heating and slow cooling preceding the quenching. Clearly the rationale of the hardening operation consists in heating the metal just through its critical range, thus conferring to it both full hardening power and finest possible structure, and then in cooling it suddenly as soon as it emerges from its range, lest its structure be coarsened by heating above the range or by prolonged exposure at the quenching temperature. This judicious method of conducting the hardening operation is sometimes described as "hardening on a rising temperature." Let it be borne in mind that, since the position and width of the critical range vary in different steels, the most desirable quenching temperature will vary likewise. Low and medium high carbon steels should be quenched at higher temperatures than high carbon steel, for in order to acquire full hardening power they should be heated past their upper critical points, namely, Ac_3 or $Ac_{3\text{-}2}$, as the case may be.

Cooling for Hardening. — To harden the steel the metal should be cooled very quickly from the temperatures mentioned in the above paragraph to atmospheric temperature, generally by immersing it in a medium capable of rapidly abstracting heat from it. The increase of hardness will be the greater the higher the carbon

content, at least up to the eutectoid point, and the more rapid the cooling, the latter, in turn, depending upon the size of the object hardened and the nature of the quenching bath, i.e. its power of abstracting heat from the cooling mass. It was long thought that this so to speak cooling power of the bath depended chiefly, if not solely, upon its temperature at the time of immersion and upon its heat conductivity. It was believed, for instance, that mercury was a more effective cooling medium than water, because of its greater conductivity for heat, that cold water was more effective than tepid water, because of its lower temperature, etc. Recent investigations appear to show, however, that the cooling power of a quenching bath is, within limits, quite independent of its actual temperature and of its heat conductivity, and even of its specific heat. Benedicks contends that it depends almost exclusively upon its latent heat of volatilization. Its temperature, however, should be low enough to

Fig. 1. — Steel. Carbon 0.45 per cent. Magnified 1000 diameters. Heated to 825 deg. C. and quenched at 720 deg. (Osmond.)

prevent the adherence of vapor bubbles to the metal. In accordance with these views mercury, in Benedicks' opinion, is inferior to water while saline solutions are not superior to it. Methyl alcohol, on the contrary, is a more effective cooling medium for hardening than water. According to Le Chatelier, also, mercury is less effective than water but in his opinion because of its lower specific heat. Le Chatelier believes that the specific heat of the liquid is the most important factor influencing its value as a cooling medium, its conductivity being of secondary importance, the loss of heat taking place more through circulation than through conductivity. On the other hand Benedicks contends that the rate of flow has very little influence.

Structural Changes on Hardening. — Bearing in mind the enormous difference between the properties of hardened steel and those of the same metal unhardened, we should naturally expect to find the structure of hardened steel likewise totally different from that of unhardened steel. And so indeed it is as shown in Figure 1, in the case of hardened steel containing some 0.50 per cent carbon. To account for this structure let us remember that, initially, this steel consisted of an aggregate of ferrite and cementite which, upon being heated through its critical

ange, was converted into a solid solution (austenite) of carbon or carbide in gamma on. This was necessary to impart hardening power. Had the metal been allowed) cool slowly through its critical range it would have been converted back into a ixture of ferrite and cementite. On rapid cooling, however, this transformation as prevented, at least in part, the time necessary for its completion having been enied. A conclusive evidence that the transformation does not occur in its entirety is fforded by the absence of a marked critical range on quick cooling. If the transforma- ion of the solid solution could be effectively prevented austenite should be the constit- ent of hardened steel. In the commercial hardening of steel, however, the cooling s not sudden enough to prevent at least a partial transformation of austenite, not nto ferrite and cementite but into a more or less transitory form, marking the first tep of that transformation and called "martensite." Very frequently the rate of

Fig. 2. — Steel. Carbon 1.57 per cent. Magnified 1000 diameters. Heated to 1050 deg. C. and quenched in ice-water. (Osmond.)

cooling is not sufficiently rapid to prevent the martensite from further partial transformation into a second transition constituent known as "troostite." Martensite and troostite, then, are the ordinary constituents of commercially hardened steel. It will now be profitable to consider at some length the occurrence, nature, and properties of the three constituents chiefly concerned in dealing with hardened steel, namely, austenite, martensite, and troostite.

AUSTENITE

Nature of Austenite.[1] — Austenite is universally considered as a solid solution of carbon or, more probably, of the carbide Fe_3C in gamma iron.[2] All steels above their critical range are made up of this solid solution. It follows that the carbon content of austenite varies, like that of steel, from a mere trace to some 1.75 or 2 per cent. It is not, therefore, a constituent of constant composition.

[1] This name was suggested by Osmond in honor of the late Sir William Roberts-Austen. Austenite has also been called mixed crystals and gamma iron and by some writers, wrongly, martensite.

[2] Arnold believes that austenite is the carbide $Fe_{24}C$ (hardenite) holding in solution ferrite in hypo-eutectoid steel and cementite in hyper-eutectoid steel.

Occurrence of Austenite. — While present in all steels above their critical range austenite is very rarely found in ordinary steels cooled to atmospheric temperature. This is due to the rapidity with which austenite is transformed on cooling through the critical range if not into an aggregate of ferrite and cementite, at least into some transition stages. In the commercial hardening of ordinary carbon steel the passage of the metal through its range is never sufficiently rapid to retain in the cold a small amount even of undecomposed austenite. To prevent the transformation of a portion of the austenite the conditions generally affecting the hardening of the metal must be, so to speak, greatly intensified: (1) the steel should be highly carburized, (2) quenching should be from a high temperature (1000 deg. C. or more), and (3) a very effective quenching bath should be used such as ice-cold water. In

Fig. 3. — Steel. Carbon 1.57 per cent. Magnification not stated. Heated to 1050 deg. C. and quenched in ice-water. (Osmond.)

Figure 2 is shown, after Osmond, the structure of steel containing 1.57 per cent carbon heated to 1050 deg. C. and quenched in ice-water. The magnification is 1000 diameters. The dark-colored, zigzag constituent is martensite; the light matrix, or background, is austenite. The structure of the same steel, under lower magnification, is seen in Figure 3. By the drastic quenching treatment just described it is possible, in the case of high carbon steel, to retain more than one half of the steel in its austenitic condition.

The retention of austenite in the cold is greatly helped by the presence of some elements such as manganese and nickel which lower the position of the transformation range, eventually depressing it below atmospheric temperature and, therefore, causing the steel to remain austenitic even after slow cooling. This actually takes place in the presence of some 12 per cent manganese or 25 per cent nickel. When high carbon steel contains over one per cent of manganese it can be retained in its aus-

tenitic condition upon very rapid cooling through its range. In Figure 4, for instance, is seen, after Robin, the structure of a very small sample of steel (1 to 2 cubic centimeters) containing from 1.5 to 1.7 per cent carbon and one per cent manganese quenched in ice-cold water from a temperature of 1400 deg. C. It consists entirely of

Fig. 4. — Steel. Carbon 1.60 per cent, manganese 1.00 per cent. Magnified 300 diameters. Heated to 1400 deg C. and quenched in ice-cold water (Robin.)

Fig. 5. — Steel. Carbon 1.94 per cent, manganese 2.20 per cent. Heated to 1100 deg. C. and quenched in ice-cold water. (Maurer.)

austenite. Maurer, likewise, succeeded in retaining in its austenitic condition a steel containing 2 per cent manganese and 2 per cent carbon by quenching it in ice-cold water from a temperature of 1100 deg. (Fig. 5). As the manganese increases the retention of austenite becomes easier, that is, the quenching need not be so drastic nor the carbon content so high. Finally with 10 or more per cent of manganese and one

or more per cent carbon the steel remains austenitic after slow cooling. The structure and properties of manganese steel will be considered in another lesson.

To sum up: (1) austenite is never produced in the commercial hardening of ordinary carbon steel; (2) it may be retained in the cold, however, associated with considerable martensite in quenching very high carbon steel, from a very high temperature in ice-cold water, as, for instance, by quenching steel containing not less than 1.50 per cent carbon from 1000 deg. C. or higher; (3) in the presence of 1 per cent of manganese very small pieces of very high carbon steel may be retained wholly in their austenitic condition by quenching them from a very high temperature, as, for instance, by quenching in ice-cold water from 1400 deg. C. small pieces of steel containing 1 per cent of manganese and not less than 1.5 per cent carbon (Robin); (4) with increasing proportions of manganese the transformation of austenite may be prevented in steel containing less carbon and quenched from lower temperatures (Maurer); (5) manganese steels containing, for instance, 10 or more per cent manganese and one or more per cent carbon remain austenitic after slow cooling; (6) nickel steel containing some 25 per cent of nickel likewise remains austenitic on slow cooling.

Benedicks contends that in the preservation of austenite in carbon steel by rapid cooling an important part is played by the very great pressure to which the metal is subjected, (1) because of the shrinkage of the exterior portion or outer shell on the interior and (2) because of the dilatation accompanying the change from gamma to beta iron. Were it not for this pressure Benedicks believes that the transformation of austenite could not be prevented. As an evidence of this he shows that austenitic steels produced by quenching are austenitic only in their interior, i.e. where the pressure had been greatest, the outside layers in which the pressure was small or nil being martensitic. He shows, further, that on removing by grinding the martensitic shell the austenitic core, in turn, becomes martensitic owing to the removal of the pressure exerted upon it by that shell. Again the quenching of steel cylinders surrounded by cast iron shells resulted in the formation of austenite close to the skin of the steel cylinders owing apparently to the very great pressure exerted upon the steel by the contraction of the iron shells.

Etching of Austenite. — The etching reagents usually applied to bring out the structure of unhardened steel, namely, picric acid, nitric acid, tincture of iodine, etc., do not always yield satisfactory results in the case of hardened steel. Kourbatoff discovered a complex reagent which often produces greater contrasts between the various constituents. It is made up by mixing one part of amyl alcohol, one part of ethyl alcohol, one part of methyl alcohol, and one part of a 4 per cent solution of nitric acid in acetic anhydride and should be prepared just before use.

Heyn recommends for etching hardened steel a solution containing one part of hydrochloric acid and 99 parts of absolute alcohol. More uniform results are obtained if a weak current of electricity be passed through the solution, the samples to be etched forming the positive pole while the negative electrode may consist conveniently of a piece of sheet lead. With the assistance of the electric current the use of a very dilute aqueous solution is advisable, namely, one part of hydrochloric acid in 500 parts of distilled water.

Osmond, likewise, used successfully a solution of 10 per cent of hydrochloric acid in water by which the martensite is colored darker than austenite, the treatment requiring several minutes. Osmond writes: "There is more regularity obtained by having the specimen connected, by means of a platinum wire, with the positive pole of a bi-chromate cell, a strip of platinum placed in the acid being connected with the

negative pole. In this way the specimen becomes the anode, and the platinum the cathode."

Benedicks recommends for the etching of martenso-austenitic steel a 5 per cent alcoholic solution of metanitrobenzol-sulphonic acid which always darkens martensite more than austenite. Immersions of some fifteen seconds are generally sufficient.

Structure of Austenite. — When austenite and martensite occur in the same sample the latter is generally colored darker than the former (Figs. 2 and 3). Martensite, moreover, is readily distinguishable because of its zigzag or needle shape. Some writers claim that martensite is sometimes colored less than austenite. Indeed Maurer contends that this is always so, arguing that if most photomicrographs indicate the contrary it is because the martensite had undergone a certain amount of tempering resulting in the formation of some troostite as later explained. According to this writer, in order to prevent any tempering of the martensite, and therefore the formation of dark-colored troostite, great care must be exercised in sawing, polishing, etc. To this Benedicks replies that it cannot always be so for in quenching austenite in liquid air martensite is formed which must be free from troostite and which, nevertheless, is darker than austenite. It may be asked, however, whether it is certain that the martensite produced in this way is actually free from troostite. Evidences of a more conclusive nature are needed to account satisfactorily for the shifting in the relative coloration of austenite and martensite when occurring side by side. Pure austenite is made up of polyhedric grains [1] (see Figs. 4 and 5) which, as explained in previous lessons in connection with the structure of gamma iron, are undoubtedly made up of true crystals, small octahedra according to Osmond. It should be noted that when austenite occurs in the presence of much martensite (Fig. 2) its polyhedric structure is not brought out. Twinnings are frequently observed in austenite (see Lesson II, Fig. 11) although it has been claimed that they form only after straining, especially if followed by annealing.

Baykoff succeeded in etching austenite above the critical range of the steel, that is, in a range of temperature where it is stable. He accomplished this by heating polished steel samples in a porcelain tube through which a current of hydrogen was kept circulating and by passing through it gaseous hydrochloric acid when the desired temperature had been obtained. The resulting structures were found to be polyhedric even in the presence of very little carbon, thus confirming the previous belief as to the crystalline character of austenite.

Properties of Austenite. — Since the carbon content of austenite varies from a mere trace to nearly 2 per cent it may well be expected that its physical properties will likewise vary, i.e. that it will increase in hardness and strength and decrease in ductility as the carbon increases. Osmond has shown conclusively that austenite was softer than martensite of identical carbon content. When it is remembered that in order to produce austenite in ordinary carbon steel all the factors generally increasing the hardness of the metal must be intensified, it is at first surprising that the energetic quenching treatment required should yield a softer metal. The conclusion must be that gamma iron is softer than beta iron. This relative softness of austenite is well shown by Osmond in Figure 6 which represents the structure of a bar of steel containing 1.55 per cent carbon in the center and a gradually decreasing amount towards the outside. This bar was heated to 1050 deg. C. and quenched in

[1] Because of this structure Guillet and some other writers refer to steels composed of austenite as "polyhedric" steels. This does not seem advisable as it may lead to confusion, for other steels also have polyhedric structures, to wit, very low carbon (ferritic) steels.

mercury at a temperature of −9 deg. C. After polishing but before etching a needle was repeatedly drawn across it from end to end with even pressure. The photograph clearly shows that the needle scratched the steel (1) where it contains so little carbon (0.40 to 0.60 per cent) that it was only partly martensitic and hence relatively soft, (2) in those regions which because of very high carbon content (1.30 to 1.55 per cent)

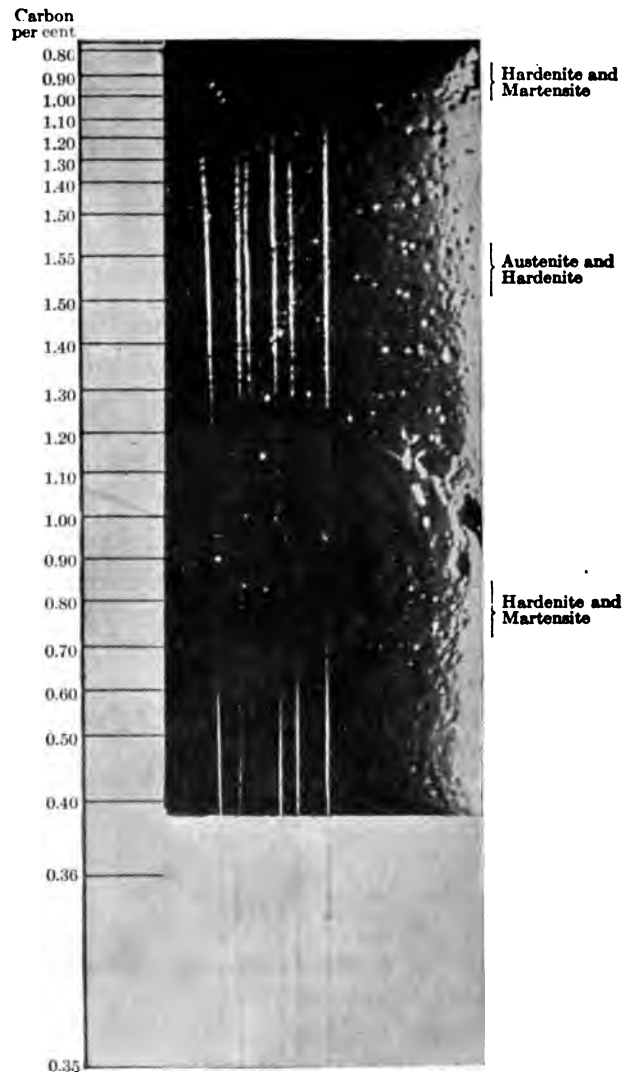


Fig. 6. — Showing the relative softness of austenite.

were partly austenitic, and (3) that it failed to scratch it in those regions which because of a more moderate amount of carbon (0.70 to 1.20 per cent) were fully martensitic and, therefore, very hard. It is also well known that high carbon austenitic manganese steel, while extremely difficult to machine, can be readily scratched by a needle, being mineralogically softer, therefore, than high carbon, martensitic steel. Rosenhain and Humphrey have shown that above the critical range austenite (gamma iron) was much softer than beta iron. Since steel above its critical range is non-

magnetic we should expect steels which remain austenitic in the cold to be non-magnetic. This we know to be the case, for manganese as well as nickel austenitic steels are non-magnetic.

Some of the physical properties of austenite may be inferred from the known properties of austenitic steels such as manganese and high nickel steels. These are known to be very ductile (after suitable heat treatment), tenacious, of low elastic limit, to possess very high resistance to wear although their mineralogical hardness is not excessive and to be machined only with great difficulty. They have, like gamma iron, a very high electrical resistance.

It has already been pointed out that the crystallization of austenite is probably

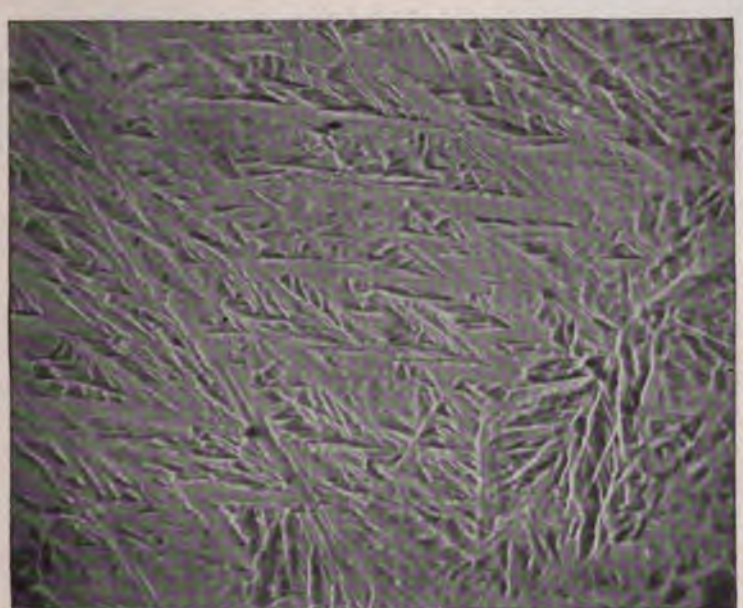


Fig. 7. — Austenitic steel quenched in liquid air. Magnified 250 diameters. (Osmond.)

cubic, the octahedron being its prevailing crystalline form. Le Chatelier, however, believes that austenite crystallizes in the orthorhombic system with octahedral cleavage. On slow cooling through the critical range in the absence of considerable quantities of retarding elements such as manganese and nickel, austenite rejects a sufficient amount of ferrite in hypo-eutectoid, or of cementite in hyper-eutectoid, steel to assume the eutectoid composition (0.85 per cent C. or thereabout) when it is converted bodily into pearlite. This transformation is not sudden, however, several transition constituents being formed, namely, martensite, troostite, and sorbite.

It will be seen in another lesson that on tempering austenite, that is, on reheating it below the critical range of the metal it is likewise converted gradually and successively into martensite, troostite, and sorbite or according to some writers directly into troostite and then into sorbite.

Quenching austenite in liquid air results in the formation of martensite with increased volume causing swellings of the polished surface as shown in Figure 7.

MARTENSITE

Nature of Martensite.[1] — It is very generally believed that martensite corresponds to an early stage in the transformation of austenite in passing through the critical range. Opinions differ, however, as to its exact nature. Accepting the possibility of iron existing under three allotropic forms, namely, as gamma, beta, and alpha iron, and the carbon under two distinct conditions, namely, as the crystallized carbide Fe_3C or cement carbon and of this carbide or possibly elementary carbon being dissolved in iron, i.e. as hardening carbon, what are the probable conditions of these two constituents in martensite? Osmond and many others believe that in martensite iron is present chiefly in its beta condition, holding carbon in solution, hence the great hardness of that constituent. Since martensite is magnetic, however, it must also contain an appreciable quantity of magnetic alpha iron. This theory, which may be called the allotropic theory, is the one most widely held. Le Chatelier, not believing in the existence of beta iron, considers martensite as essentially a solid solution of carbon in alpha iron, owing its great hardness to its state of solid solution and its magnetism to the presence of alpha iron. Edwards contends that austenite and martensite are in reality the same constituent, namely, a solid solution of carbon in gamma iron, differing only in structural aspect, the needles of martensite resulting from the twinning of austenite caused by the severe pressure exerted upon it during rapid cooling. He bases his view chiefly upon the absence of the point A_2 in medium high and high carbon steels, from which he infers that beta iron does not form in those steels, losing sight of the fact that the points $A_{3.2}$ and $A_{3.2.1}$ may very well, and probably do, include the A_2 changes. Kroll also speaks of martensite as representing the "mutilated structure of austenite due to twinning." Arnold believes that martensite is, like austenite, the carbide $Fe_{24}C$ holding in solution ferrite in hypo-eutectoid steel and cementite in hyper-eutectoid steel.

Careful consideration of the evidences at hand leads to the adoption of the first theory (Osmond's) as the one best supported. That martensite is to a great extent a solid solution seems evident from the fact that it contains a great deal of hardening, i.e. dissolved carbon, and it seems probable that beta iron is the solvent, for if gamma iron were the solvent it would not explain the greater hardness of martensite compared to that of austenite while we have good reason to doubt the power of alpha iron to dissolve carbon seeing that below the critical range, i.e. when in its alpha form, iron will not absorb carbon.

Occurrence of Martensite. — Martensite is most readily obtained through the quenching of small pieces of high carbon steel in cold water; in the case of large pieces, while the outside portion may be martensitic their center is likely to be partly troostitic. In low carbon steel it is more difficult still to prevent the formation of some troostite while in steel containing very little carbon free ferrite as well is likely to be present. In very high carbon steel some free cementite is generally associated with the martensite.

Etching of Martensite. — Dilute alcoholic solutions of picric, nitric, or hydrochloric acid generally bring out satisfactorily the structure of martensite but the Kourbatoff reagent, already described, sometimes yields better results. Martensite generally darkens more quickly than austenite but always remains much lighter than troostite.

[1] This name was selected by Osmond in honor of A. Martens a distinguished German metallurgist and testing engineer.

Structure of Martensite. — Martensitic structures are shown in Figures 1 and 8. Osmond describes the structure of martensite as consisting of three systems of fibers, respectively parallel to the three sides of a triangle and crossing each other frequently. Osmond also states that when the metal contains less carbon the needles are longer and more clearly differentiated, other things being equal. According to crystallographers these markings, in reality cleavages of octahedra, indicate crystallites of the cubic system and, therefore, afford an additional evidence of the cubic crystallization of austenite from which martensite is derived. Osmond and Cartaud refer to them as probable pseudomorphs of twinnings due to tension, occurring in gamma iron through partial formation of the bulky beta and alpha modifications.

Properties of Martensite. — The carbon content of martensite varies from a mere trace to as much as one per cent, and possibly more, in very suddenly cooled hypereutectoid steels. In high carbon steels, however, it is difficult to prevent the setting

Fig. 8. — Steel. Carbon 1.25 per cent. Magnified 150 diameters. Heated to 1232 deg. C. and quenched in oil. (C. C. Buck, Correspondence Course student.)

free of much of the excess cementite even on very quick cooling. From this variation of its percentage of carbon it follows that the properties of martensite must also vary. As the carbon increases its hardness and strength increase while its ductility decreases, martensitic steels being generally hard and brittle and, therefore, unforgeable in the cold.

It will be seen in another lesson that on heating martensite below the critical range, i.e. on tempering it, it is converted first into troostite and then into sorbite.

TROOSTITE

Nature of Troostite.[1] — While most writers believe that troostite represents a condition of the steel resulting from the transformation of martensite and, therefore, a further step in the transformation of austenite, much difference of opinion exists as to its exact nature. The controversy has given rise to a very large and apparently exaggerated amount of discussion. Here, as in the case of martensite, we must con-

[1] The name troostite was selected by Osmond in honor of the French chemist Troost.

sider the possibility of the iron existing in the gamma, beta, or alpha form or in two or even all three of these conditions, while the carbon may exist as cement carbon or as hardening carbon or partly as cement and partly as hardening carbon. Then the association between iron and carbon may be of the nature of an aggregate or of a solid solution or partly aggregate and partly solution, or, indeed, half way between aggregate and solution, namely, resembling a colloidal solution, an emulsion, or an uncoagulated substance. Nearly every conceivable hypothesis has been suggested to account for the nature of troostite. It has been described as a solid solution of carbon or of carbide in gamma iron, in beta iron, and in alpha iron. It has also been suggested that it might be pure beta iron.

In later years, thanks chiefly to the enlightening discussions of Benedicks supported by the weighty evidence of skilfully conducted experiments, metallographists have come to regard troostite as an uncoagulated mixture of the constituents of martensite and sorbite, that is, of (1) carbide dissolved in beta iron, (2) crystallized Fe_3C, and (3) crystallized alpha iron — clearly martensite passing to sorbite. Benedicks compares it to a colloidal solution[1] while Arnold had previously described it as "emulsified" pearlite.[2] The existence of considerable dissolved (hardening) carbon in troostite is proven by analysis as well as the existence of considerable crystallized Fe_3C (cement carbon). Its relatively great hardness points strongly to the presence of a considerable amount of beta iron while its magnetism demands the presence of alpha iron. Benedicks' hypothesis is consistent with what we know of the formation of troostite and of its properties.

In the report of the Committee on the Nomenclature of the Microscopical Constituents of Iron and Steel of the International Association for Testing Materials, troostite is defined as follows: "probably aggregate. In the transformation of austenite, the stage following martensite and preceding sorbite . . . An uncoagulated conglomerate of the transition stages."

Occurrence of Troostite. — In order to produce troostite on cooling steel from above its critical range, it is necessary that the cooling through the range should be so regulated as to allow it to form and at the same time prevent its further transformation (into sorbite and pearlite). These conditions may prevail (1) in cooling slowly to the middle of the range, thus permitting the formation of troostite (see Fig. 13), and then quickly to atmospheric temperature, thus retaining troostite, and (2) in cooling through the range at a rate uniform throughout but so regulated as to cause the production and retention of troostite (Fig. 13) as, for instance, quenching large pieces in water when the central portions at least will be troostitic, or quenching smaller pieces in oil. It will be explained in the next lesson that troostite may also be produced by tempering (i.e. reheating below the critical range) austenitic and martensitic steels.

Troostite is readily produced by heating a bar of steel, containing 0.50 per cent carbon or more, white hot at one end and quenching it in water, when at some distance from the heated end the temperature must necessarily have been such as to produce troostite. This can generally be detected by means of a file, the martensitic

[1] A colloid may be regarded as a substance passing from the state of solution to that of an aggregate or vice versa; it is no longer a solution but not yet an aggregate. To express it more scientifically, while not a true solution the particles of solvent and solute are ultra-microscopic. According to Le Chatelier so-called colloidal solutions are in no way solutions, but merely liquids holding in suspension very finely divided particles; the expression, he says, should not be used.

[2] "Emulsified carbide present in an excessively fine state of division in tempered steels." (1895.)

portion of the bar being too hard to be marked while the troostitic part, although hard, can be scratched. The sorbitic and pearlitic portions are decidedly softer.

Properties of Troostite. — It will be obvious from the foregoing description of the nature and formation of troostite that its physical properties must be intermediate between those of martensite and of sorbite. For like carbon content troostite is softer and more ductile than martensite but harder and less ductile than sorbite. It will be shown that at some 400 deg. C. it begins to be transformed into sorbite.

Etching of Troostite. — Troostite is colored decidedly darker than any other constituent by the ordinary etching reagents. While dilute alcoholic solutions of nitric, picric, or hydrochloric acid yield satisfactory results, Kourbatoff's reagent is preferred by some.

Structure of Troostite. — Troostite generally occurs as dark-colored, irregular areas, representing sections through nodules generally accompanied by martensite or

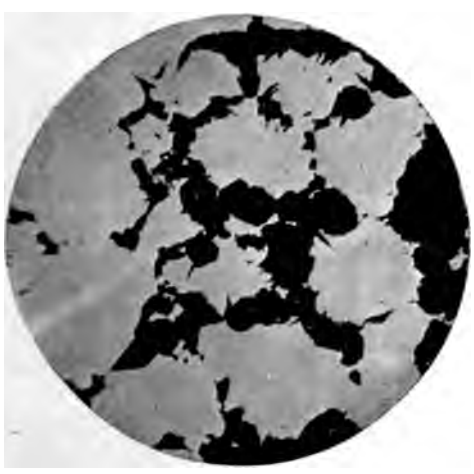


Fig. 9. — Steel. Quenched during critical range. Magnified 200 diameters. Slightly etched. Troostite and martensite. (Guillet.)

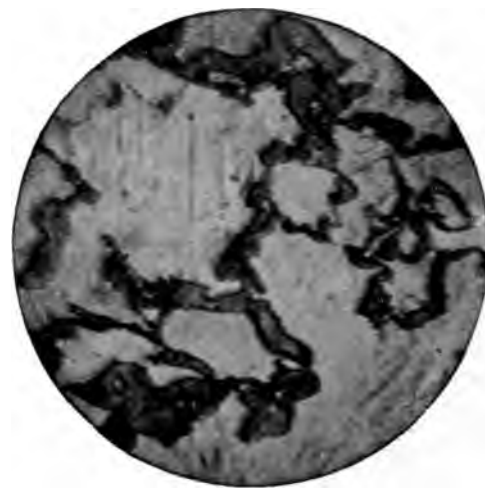


Fig. 10. — Steel. Carbon 0.45 per cent. Magnified 1000 diameters. Troostite and martensite. (Osmond.)

sorbite or both or as membranes surrounding martensite grains (Figs. 9 to 12). In hypo-eutectoid steel free ferrite, and in hyper-eutectoid steel free cementite, may also be present and, indeed, even well-developed pearlite (Fig. 12). Osmond describes the structure of troostite as "almost amorphous, slightly granular, and mammilated."

Sorbite. — Sorbite is not, properly speaking, a constituent of hardened steel. It seems appropriate, however, to again mention it here seeing that it constitutes the connecting link between annealed (pearlitic) steels and hardened (troosto-martensitic) steels, and also because it results from the transformation of troostite, thus completing the various stages assumed by iron carbon alloys in passing from the condition of austenite, stable above the range, to that of pearlite, stable below that range. These stages are (1) austenite, (2) martensite, (3) troostite, (4) sorbite, and (5) pearlite.

Sorbite is now generally regarded as an uncoagulated mixture of the constituents of troostite and of pearlite; it apparently contains (1) some hardening carbon, i.e. carbon or Fe_3C dissolved in beta iron, hence the greater hardness and strength of sorbite compared to the hardness and strength of pearlite, (2) a considerable quan-

tity of alpha iron, hence its magnetism and relative softness, and (3) a considerable quantity of crystallized Fe_3C (cement carbon) as proven by analysis. While sorbite probably contains the same constituents as troostite it holds considerably less undecomposed solid solution and considerably more alpha iron, hence it is much softer

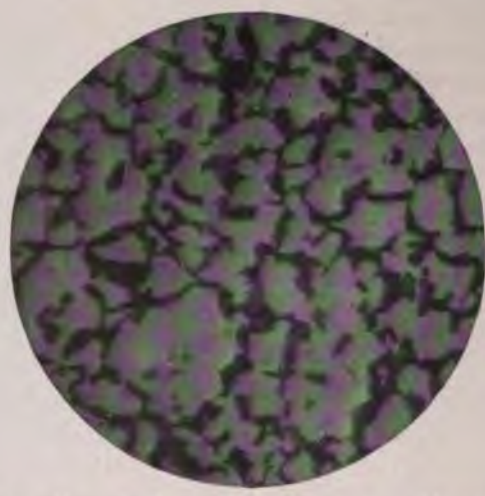


Fig. 11. — Steel. Carbon 0.54 per cent. Magnified 100 diameters. Troostite and martensite. (Boynton.)

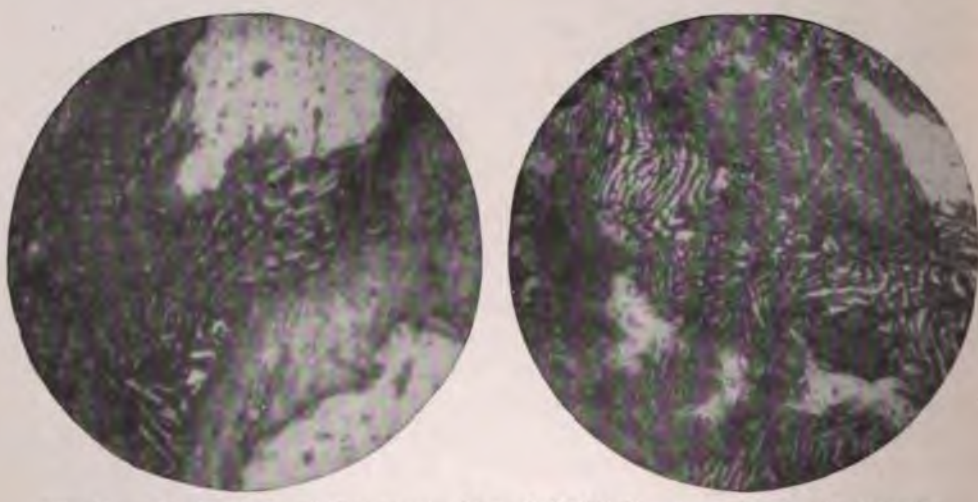


Fig. 12. — Steel. Carbon 0.54 per cent. Magnified 1000 diameters. Martensite, troostite, sorbite, and pearlite. (Boynton.)

and more ductile than troostite. In other words the transformation which eventually must lead to the formation of pearlite is more advanced in sorbite than it is in troostite. The nomenclature committee, already referred to, describes sorbite as follows: "Aggregate . . . In the transformation of austenite, the stage following troostite . . . and preceding pearlite. Most writers believe it essentially an uncoagulated conglomerate of irresoluble pearlite with ferrite in hypo- and cementite in hypereutectoid steels respectively."

The occurrence, etching, structure, and properties of sorbite have been described in Lessons XI and XII when it was shown that it is formed (1) in small pieces of steel cooling in the air from above their critical range, (2) in larger pieces quenched in oil from above the range, or (3) in small pieces quenched in water from near the bottom of the range. In other words to form sorbite we must so regulate the cooling through the critical range that it is allowed to form but prevented from further transformation (into pearlite). It will be seen in the next lesson that sorbite is also formed on tempering austenitic, martensitic, and troostitic steels.

By its physical properties sorbite occupies an intermediate position between troostite and pearlite; as previously mentioned it is stronger, harder, and less ductile than pearlite but softer and more ductile than troostite.

Troosto-Sorbite. — Kourbatoff gives the name of troosto-sorbite to a constituent associated with martensite and austenite in quenching, from a high temperature, steels very high in carbon. It is not clear that this constituent is more than a mixture of troostite and sorbite. We may talk of troosto-sorbite as we do of a greenish blue tint to indicate shades intermediate between green and blue, and similarly the expressions martenso-austenite, troosto-martensite, and sorbitic-pearlite, or like expressions, are useful and their meanings obvious. In the report of the Committee on the Nomenclature of the Microscopical Constituents of Iron and Steel of the International Association for Testing Materials, troosto-sorbite is thus defined: "Indefinite aggregate, the troostite and the sorbite which lie near the boundary which separates these two aggregates."

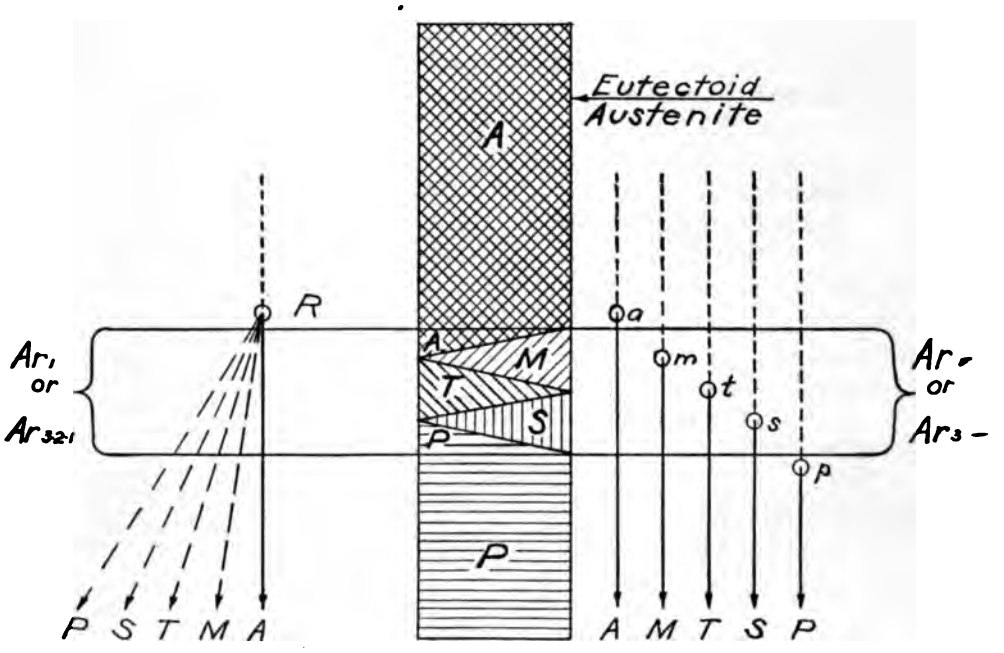
Hardenite. — The name of hardenite is frequently given both to austenite and to martensite of eutectoid composition,[1] i.e. to the original austenite of eutectoid steel and to the residual austenite of hypo- and hyper-eutectoid steel after rejection of the full amount of free ferrite or of free cementite. In other words the name is applied (1) to the condition of austenite in slowly cooled steels immediately preceding its conversion into martensite and (2) to the resulting martensite (necessarily of eutectoid composition if the cooling to the range has been sufficiently slow). It is unfortunate that the same term is used to designate both austenite and martensite, two apparently sharply different constituents, as it is likely to lead to confusion. Its use should be restricted to the designation of austenite of eutectoid composition. Giving it this meaning it will be apparent, as later explained, that hardenite possesses maximum hardening power and, therefore, that steel made up exclusively of hardenite, i.e. eutectoid steel, possesses maximum hardening power.

Rate of Cooling through Critical Range vs. Structure of Steel. — It has been made clear in the foregoing pages (1) that in order to retain some austenite in the cold the metal should be highly carburized and very quickly cooled from a high temperature, (2) that pearlite is produced by very slow cooling through the critical range, and (3) that in order to cause the formation of any of the three recognized transition constituents, namely, martensite, troostite, and sorbite, the steel should be cooled through its critical range in such a way as to allow the formation of the desired constituent while preventing its further transformation as, for instance, (*a*) by cooling the metal slowly to that portion of the range in which the constituent is formed and then quickly to atmospheric temperature or (*b*) by cooling the metal through its range at a uni-

[1] Originally the name hardenite was applied by Howe to austenite and martensite of any composition (1888). Osmond used it to designate austenite saturated with carbon (1897). Both these meanings have been withdrawn by their proposers. Arnold calls hardenite the carbide $Fe_{24}C$ which he believes exists above the critical range.

form speed but so regulated that the transformation of austenite proceeds only to the desired extent, to wit, cooling in water for martensite, in oil for sorbite.

An attempt has been made in Figure 13 to give a graphical illustration of the cooling conditions needed for the production of the various constituents of steel. Its interpretation will be obvious. The critical range, or rather the lower critical point, Ar_1 or $Ar_{3.2.1}$ is represented as covering a considerable range of temperature so as to afford the necessary room for the diagrammatical representation of the formation, within that range, of the transition constituents. The diagram indicates that as the metal cools slowly through its range it does not pass abruptly from an austenitic to a martensitic condition and then to troostite, etc., but that these transformations



A = Austenite
M = Martensite
T = Troostite
S = Sorbite
P = Pearlite

Fig. 13. — Diagram depicting the formation of austenite, martensite, troostite, sorbite, and pearlite in steel cooling through its critical range.

are, on the contrary, gradual, the following types of structure being formed, theoretically at least: austenite, austenite plus martensite, martensite, martensite plus troostite, troostite, troostite plus sorbite, sorbite, sorbite plus pearlite, and pearlite. The transformations depicted refer to eutectoid steel or to the residual austenite (necessarily of eutectoid composition) of hypo- and hyper-eutectoid steel formed on slow cooling to Ar_1 after rejection of free ferrite or free cementite. In the cases of these steels, therefore, free ferrite or free cementite is present in the above structures, unless, indeed, cooling between Ar_3 and Ar_1 or between Ar_{cm} and Ar_1 has been so rapid as to prevent their separation. While, theoretically, very quick cooling from *a* to atmospheric temperature should retain the steel in its austenitic condition, even under the most favorable conditions, this can be done but partially, considerable martensite being produced. Cooling slowly to *m* and then quickly should produce martensite

while slow cooling to t or s followed by quick cooling should produce, respectively, troostite and sorbite. Slow cooling to p, followed or not by quick cooling, results in the formation of pearlite. Slow cooling to intermediate points between m and t or t and s, etc., should, theoretically, cause the formation of martensite and troostite, troostite and sorbite, etc.

These conditions may be realized in the same piece of steel by heating one end of a steel bar, preferably of eutectoid or hyper-eutectoid composition, well above the critical range and quenching the whole bar in ice-cold water. It is evident that, since at the time of quenching the temperature of the bar decreased gradually from the hot to the cold end, a portion of the bar must have been quenched while in the martensitic condition, another while in the troostitic condition, etc. The preparation and microscopical examination of longitudinal sections through the center of the bar should reveal the existence of the various constituents indicating as many stages in the transformation of austenite.

On the left of the diagram five lines starting from the point R above the critical range represent coolings through the range at different speeds as, for instance, (1) very quickly in ice-cold water, (2) quickly in water, (3) less quickly in oil, (4) slowly in air, and (5) very slowly in furnace, resulting, respectively, in the formation of austenite (or rather austenite and martensite), martensite, troostite, sorbite, and pearlite or, more frequently, of mixtures of two or even three of these constituents.

These conditions may be realized in the same piece of metal by heating a steel bar of considerable cross section (not less than one inch in diameter) and preferably of eutectoid or hyper-eutectoid composition to a temperature well above the critical range and quenching it in water. The cooling should be rapid enough to cause the formation of martensite near the outside of the piece while the cooling of the center should be so slow (because of the size of the bar) as to permit the formation of pearlite. Between the martensitic shell and the pearlitic core the metal should be composed of the other transition constituents, that is, starting from the center, of sorbite and then of troostite. The microscopical examination of a cross section through the bar should reveal this gradual change of structure from center to outside.

The formation of a transition constituent through the tempering of a constituent representing a less advanced, and therefore less stable, stage of transformation has already been alluded to and will be considered at greater length in the next lesson.

Are the Transition Stages Distinct Constituents? — It would appear from our consideration of the formation of the transition constituents that they must represent as many stages in the *progressive* transformation of austenite and that sharp lines of demarcation between them are not to be expected or, rather, that they must be linked together by an unbroken chain of transition stages just as the blue and yellow colors are connected through an unbroken series of bluish, greenish, and yellowish shades. This logical inference, however, is not supported by microscopical evidences in the cases of austenite, martensite, and troostite for these constituents are sharply differentiated from each other whenever they occur together. Stages or structural conditions representing the gradual transformation of austenite into martensite or of martensite into troostite are not observed; it is as if these transformations had actually taken place by rather sudden steps.

The transformations of troostite into sorbite and of sorbite into pearlite, on the contrary, appear to be very gradual and easy to follow. In other words while troostite, sorbite, and pearlite are readily distinguishable, each having marked charac-

teristics of its own, structural arrangements are frequently observed which undoubtedly correspond to intermediate stages.

The five constituents of steel, resulting from various modes and rates of cooling, might be compared to a spectrum of five elementary colors, i.e. violet, blue, yellow, orange, and red, with gaps existing between the first three (our austenite, martensite, and troostite) while the third and the fifth, yellow and red (troostite and pearlite) are closely linked together by the fourth, orange (our sorbite), and an infinity of intermediate shades.

Metarals and Aggregates. — Howe suggests dividing all microscopical constituents of iron and steel into (1) metarals and (2) aggregates.

These he describes as follows: "Metarals, true phases like the minerals of nature. These are like definite chemical compounds, or solid solutions, and hence consisting of definite substances in varying proportions . . . Aggregates, like the petrographic entities as distinguished from the true minerals. These mixtures may be in definite proportions, i.e. eutectic or eutectoid mixtures (ledeburite, pearlite, steadite) or in indefinite proportions (troostite, sorbite)." [1] Under these two headings the constituents of iron-carbon alloys would be classified as follows:

Metarals: ferrite, cementite, austenite, graphite.

Aggregates: pearlite, sorbite, troostite, ledeburite, steadite.

Opinions differ as to the nature of martensite; if it is a solid solution it is a metaral, if not it must be classified with the aggregates. Should we recognize the existence of solid colloidal solutions, it is not clear whether these should be grouped with the metarals or should form a distinct class between the metarals and the aggregates.

Hardening Eutectoid Steel. — It will now be profitable to consider separately the hardening of eutectoid, hyper-eutectoid, and hypo-eutectoid steel. In hardening eutectoid steel the metal should be heated through its critical range, i.e. through its single critical point $Ac_{3.2.1}$. By so doing we confer upon it full hardening power and finest possible structure. The steel should then be cooled from that temperature as promptly as possible avoiding heating much above the range or long exposure at any temperature above the range, as either procedure would tend to increase the grain size of the metal. A temperature of some 775 to 825 deg. C. will generally be, therefore, the best temperature to which to heat and from which to cool eutectoid steel for the purpose of hardening. By this treatment the steel passes from a finely austenitic to a finely martensitic or troosto-martensitic condition (Fig. 8).

Hardening Hyper-Eutectoid Steel. — Let us assume a steel containing 1.25 per cent carbon and, therefore, composed approximately of 93 per cent of pearlite and 7 per cent of free cementite. Upon heating this steel through its lower point $Ac_{3.2.1}$ its 93 per cent of pearlite are converted into 93 per cent of austenite possessing hardening power, but the metal still contains 7 per cent of free cementite deprived of hardening power. If we heat it past its upper point Ac_{cm} the free cementite is absorbed and the whole mass becomes austenitic. A little reflection will show, however, that the steel should be quenched as soon as it rises above the point $Ac_{3.2.1}$, because we then produce, theoretically at least, 93 per cent of fine grained martensite while retaining, to be sure, the original 7 per cent of cementite, but as this constituent is harder than

[1] Howe further writes: "Many true minerals, such as mica, felspar, and hornblende, are divisible into several different species. Such minerals are definite chemical compounds, in which one element may replace another. Others, such as obsidian, are solid solutions in varying proportions and in these also one element may replace another. Metarals like minerals differ from aggregates in being severally chemically homogeneous."

martensite its presence adds to, rather than takes away from, the hardness of the quenched metal. Should we, on the contrary, heat to above Ac_{cm} before quenching the whole mass would be converted into martensite but it would be less hard if anything than the metal quenched at a lower temperature while its structure would be coarser and the danger of cracking the objects in the quenching bath would be greater. The best hardening temperature for hyper-eutectoid steels, therefore, is the same as that for eutectoid steel, namely, some 775 to 825 deg. C.

The structure of a properly hardened hyper-eutectoid steel is shown in Figure 14. Like hardened eutectoid steel it consists of very fine martensite.

Hardening Hypo-Eutectoid Steel. — Let us take a steel containing some 0.50 per cent carbon and exhibiting therefore the points A_1 and $A_{3.2}$. Such steel is made up

Fig. 14. — Steel. Carbon 1.10 per cent. Magnified 100 diameters. Quenched in water from above its critical range. (Boylston.)

of 60 per cent of pearlite and 40 per cent free ferrite. Upon heating it through its Ac_1 point the pearlite is converted into austenite, so that at this temperature some 60 per cent of the mass of the metal is endowed with hardening power. Should we quench this steel, therefore, as soon as it rises above its lower critical point but 60 per cent of its bulk would be hardened; it would still retain 40 per cent of soft ferrite. If, on the contrary, the heating be carried to just above $Ac_{3.2}$ the free ferrite is absorbed by the austenite and the whole mass becomes *hardenable*. Upon quenching the steel from that temperature its entire bulk may be converted into martensite or troosto-martensite, according to rate of cooling. While this martensite will not be quite as hard as the martensite produced by quenching from just above Ac_1 the metal as a whole will be harder and of a more uniform and finer structure because of the absence of free ferrite, or at least of any considerable amount of it. It follows from these considerations that for the purpose of hardening, hypo-eutectoid steel should be quenched from just above its upper critical point, namely, $Ac_{3.2}$ or Ac_3 (825 to 925 deg. C. according to carbon content). Hypo-eutectoid steel containing very little carbon, say

less than 0.25 per cent, cannot be very materially hardened by the ordinary quenching methods because of the large amount of soft ferrite which it contains in excess of the eutectoid ratio and which cannot be retained in solution, even on very quick cooling (see Lesson XII, Fig. 11). The structure of hardened hypo-eutectoid steel is shown in Figure 1.

Steel of Maximum Hardening Power. — From the above considerations it will be obvious that the hardening of steel consists in preventing the formation of relatively soft pearlite and in causing, instead, the formation and retention of hard martensite or troostite or, more often, of both. It follows from this that the steel possessing maximum hardening power must be that steel which in slow cooling would contain most pearlite, namely, eutectoid steel. It does not, of course, mean that quenched eutectoid steel is harder than quenched hyper-eutectoid steel but merely that the increased hardness produced by quenching is greatest in the case of eutectoid steel. Quenched hyper-eutectoid steel is harder than quenched eutectoid steel because of the presence in the former of some free cementite or of more highly carburized martensite but the difference of hardness between the two steels is greater before quenching.

Hardening Large Pieces. — In hardening pieces of considerable cross section it is evident that the central portions will not cool as quickly as the outside and will not, therefore, be as hard. Indeed the center may cool so slowly that it will fail to harden at all. The limitation of the hardening process, as applied to large pieces, will, therefore, be evident. It is seldom desirable, however, to harden large pieces to their very core. When large steel objects are to be hardened, as for instance in the case of armor plates, superficial hardness only is desired, or at least hardness penetrating to but a relatively small depth, and this is readily secured through the case hardening process.

Hardening and Tempering in One Operation. — A peculiar but frequent way of hardening tools consists in heating the tool to the proper temperature and then cooling quickly to a black heat only that portion of it which should be hard, while keeping the other portion out of the bath and, therefore, at a high temperature. Upon withdrawing the tool from the bath the heat stored away in the hot portion diffuses to the cooled portion which is in this way reheated, that is, tempered, as later explained, the amount of tempering being regulated at will by again quenching the metal as soon as the desired tempering color has been obtained.

Experiments

The following experiments will prove instructive. A steel bar about one half inch square or round and containing some 0.50 per cent carbon should be heated at one end, conveniently in a forge, in such a way that the extreme end will be at a very bright red or yellow heat while its color three inches from the end should not be more than a very dull red. The whole bar should then be quenched in cold water. Three pieces one inch long should be detached from the heated end of the bar and a longitudinal section of each piece polished, etched, and microscopically examined. Starting with the piece that was heated to the highest temperature the constituents of hardened steel should be noted in the ordinary order, i.e. martensite, troostite, sorbite, and in the unhardened portion, pearlite, or association of two or more of these. Free ferrite will occur, of course, in the pearlitic portion while it may also be observed, but in smaller quantity, in the sorbitic and even troostitic zones.

Small pieces of hypo-eutectoid, eutectoid, and hyper-eutectoid steels should be

heated above their respective critical range and quenched in cold water and some in oil. Cross sections of all pieces should be prepared for examination which should show that the pieces quenched in water are martensitic or troosto-martensitic while those quenched in oil are chiefly troostitic or troosto-sorbitic. In hypo-eutectoid steel free ferrite and in hyper-eutectoid steel free cementite are likely to occur.

If a sample of steel can be obtained containing not less than 1.50 per cent carbon and not less than 1 per cent manganese (preferably 2 per cent) a small piece of this steel should be heated to 1100 deg. C., or higher, and quenched in ice-cold water. This treatment should produce a martenso-austenitic structure.

Etching. — The reagents already described for etching pearlitic and sorbitic steels, namely, solutions of nitric and picric acid in alcohol, may be employed with generally satisfactory results for the etching of hardened steels. As these etch much more quickly, however, the immersions should be correspondingly shorter, especially when the metal contains troostite. Picric acid being slower in its action than nitric acid is preferred by some for etching hardened steel. The Kourbatoff reagent may be tried.

Examination

I. — Describe the treatment necessary to impart hardening power to steel.

II. — Explain the influence of the rate of cooling through the critical range on the structure of steel and describe briefly the constituents resulting from cooling through that range at various speeds.

LESSON XIV

THE TEMPERING OF HARDENED STEEL

Steel that has been hardened by rapid cooling from above its critical range, as explained in the preceding lesson, is often harder than necessary and generally too brittle for most purposes. In order to decrease its brittleness, that is, to toughen it without very material diminution of hardness, the metal is generally "tempered," that is, reheated to a temperature considerably below its critical range. This operation is called tempering because it somewhat mitigates or tempers the effects of the previous hardening treatment.

Tempering Temperatures. — The hardening of steel causes increased hardness, brittleness, and elastic limit, all of which are somewhat lowered by the tempering operation. The effect of tempering begins to be noticeable at about 100 deg. C. and increases in intensity as the temperature rises, until finally at some 600 deg. the metal assumes again the physical properties characteristic of the unhardened condition. The temperature to which hardened steel should be heated for tempering varies, therefore, with the use to which it is destined. If it is desired to retain the greatest possible hardness, necessarily with its accompanying brittleness, the steel should be reheated but slightly above 200 deg. C., as, for instance, in tempering razor blades when extreme hardness is essential and brittleness relatively immaterial. If, on the contrary, considerable toughness is indispensable, at the necessary sacrifice of some hardness the steel should be tempered to some 300 deg. C. or even to a higher temperature. The great majority of tools are tempered between 200 and 300 deg.

Tempering Colors. — Hardened steel objects subjected to tempering being generally quite bright and their heating being generally conducted in an oxidizing atmosphere, very thin films of oxides form upon their surfaces. The colors of these films vary with the temperature, that is, to each tempering temperature corresponds a certain color, and blacksmiths generally depend upon these colors for the tempering of their tools, the use of pyrometers for this operation being far from general. According to Howe the tempering colors and corresponding temperatures are as follows:

Pale yellow	220 deg. C. or	428 deg. F.
Straw	230 " " "	446 " "
Golden yellow	243 " " "	469 " "
Brown	255 " " "	491 " "
Brown dappled with purple	265 " " "	509 " "
Purple	277 " " "	531 " "
Bright blue	288 " " "	550 " "
Pale blue	297 " " "	567 " "
Dark blue	316 " " "	600 " "

In order that the tempering colors may be plainly seen the steel objects should be smooth and bright, preferably polished.

Time at Tempering Temperature. — It is the common belief that once the desired temperature is obtained, as indicated by the color, little is to be gained by maintaining

the steel at that temperature any length of time on the ground that it will not result in producing additional tempering. The tempering of steel has been compared to the releasing of a spring permitting a certain structural rearrangement, that is, a certain tempering of the metal at any temperature but not more. To produce additional tempering the temperature must be increased, that is, the spring must be further released. Recent investigations, however, have shown that the maintenance of hardened steel at a certain tempering temperature often does produce additional tempering effect. It was further ascertained that the color, instead of remaining unchanged at any given temperature, advances in the tempering color scale as it would with increasing temperature. In other words, the tempering colors, contrary to the view generally held, are not an absolute criterion by which to judge of the temperature of the steel, since they vary with the length of time during which the steel is kept at any temperature. These experiments seem to show, however, that the amount of tempering effected is closely related to the color, that is, that to each shade corresponds a certain amount of tempering. It should, however, be borne in mind that these colors, with the corresponding tempering they imply, may be obtained in two ways, (1) through short exposure at a certain temperature and (2) through longer exposure at lower temperatures. The same amount of tempering, for instance, would result (*a*) from heating hardened steel to 288 deg., when its color is bright blue, followed by immediate cooling and (*b*) from heating it to 255 deg., when its color is brown, and maintaining it at that temperature until its color becomes bright blue. Unless baths kept at constant temperatures are used, however, it is evident that in practise the steel should be quenched as soon as the desired color is produced and while its temperature is rising, because it is simpler and more convenient to produce that color on a rising temperature than by maintaining the metal at a constant temperature.

Some writers doubt the existence of so close a relation between the color and the resulting tempering. According to Barus and Strouhal to each tempering temperature corresponds a maximum tempering effect which is the more quickly reached the higher the temperature. At 100 deg., for instance, the maximum effect was not obtained after one hour although maintaining the steel at that temperature two more hours had but little additional effect. At 200 deg. the maximum effect was obtained in ten minutes, while at 300 deg. one minute was sufficient.

Rate of Cooling from Tempering Temperature. — Once the desired amount of tempering is effected, as indicated by the color or otherwise, the rate of cooling to atmospheric temperature appears to be quite immaterial. In practise the piece is generally quenched, merely for convenience. The theory is that while by keeping the metal at a certain temperature its tempering may be carried farther, on cooling tempering ceases, for the spring is now tightened, to use the simile already referred to, so that the rate of cooling is without influence.

Hardening and Tempering Combined. — A method of hardening and tempering combined, frequently employed when but one end of a tool must be hardened as in the case of chisels and drills, has been described in the preceding lesson. It consists in heating the tool above its critical range, quenching that portion only which is to be hard, removing it from the bath, and allowing the heat stored in the unquenched portion to heat by conduction the quenched part until the desired temper color is obtained, when it is again quenched lest the tempering be carried too far.

Explanation of the Tempering of Steel. — The theories accounting for the tempering of steel will be considered in the next lesson together with the hardening theories. It will suffice for the present to point out that hardened steel is generally considered

to be in an unstable condition and, therefore, eager to return to a more stable form and actually undergoing this change whenever given an opportunity, that is on raising its temperature. At atmospheric temperature the passage of an unstable martensitic condition into a more stable troostitic or sorbitic form is prevented by the rigidity of the metal. A slight heating, however, produces some plasticity and such transformation takes place to a small extent. On increasing the temperature the rigidity diminishes farther and the transformation advances. The tempering of hardened steel, in other words, is due to its transformation from an unstable condition to one more stable. It will be seen that at some 600 deg. C. the metal assumes a stable condition, i.e. is fully tempered.

Tempering Austenitic Steels. — It has been explained in the preceding lesson that austenite, martensite, troostite, and even sorbite were the constituents formed in hardened steel according to the rapidity with which the metal is cooled through and below its critical range. It will now be instructive to consider separately the tempering of steels having these different types of structure.

Austenitic carbon steel, as already stated, is not a commercial article, as it requires for its production, at least in the absence of a large proportion of manganese, the presence of much carbon, an excessively high quenching temperature, and a quenching bath at a very low temperature. And even when these conditions prevail, only one half or so of the bulk of the steel can be retained in an austenitic condition, the other half being martensitic. The tempering of austenite should, nevertheless, be considered. Since in austenitic steel the condition of the metal stable only above the critical range has been retained in the cold, it follows that cold austenitic steel must be in a very unstable condition. At atmospheric temperature the rigidity of the metal is so great that a return to a more stable form is not possible but, on heating it very slightly, sufficient plasticity is produced to permit a partial transformation of austenite. This partial transformation, theoretically at least, should result in the formation of martensite, troostite, and sorbite in the order named as the tempering temperature increases. This has been depicted in I, Figure 1. In this diagram it is shown (1) that as soon as austenite is heated above atmospheric temperature it begins to be converted into martensite, (2) that it is entirely converted into martensite at 200 deg. C., (3) that in heating above 200 deg. martensite begins to pass to troostite, (4) that at 400 deg. the transformation of martensite into troostite is complete, (5) that above 400 deg. troostite is gradually converted into sorbite, (6) that at 600 deg. C. the transformation of troostite into sorbite is complete, and (7) that the sorbite condition is the final condition acquired by hardened steel when reheated close to, but below, its critical range. While it is certain that lamellar, i.e. true pearlite, cannot be formed by reheating hardened steel, it is claimed by some that long heating of sorbite near the critical range, that is, between 600 and 700 deg. C., will result in the formation of granular pearlite brought about as explained in another lesson by the spheroidizing of the cementite. The tempering of austenite depicted in I, Figure 1, represents the transformation which, according to theoretical consideration, should be expected to take place. Most observers, however, report that on tempering austenite it is at once converted into troostite as soon as the rigidity of the steel has been sufficiently relaxed, the martensitic stage not being assumed. This is shown diagrammatically in II, Figure 1. Here, again, it is indicated that at 400 deg. the steel is entirely troostitic and at 600 deg. entirely sorbitic. Benedicks thinks that it is quite possible that austenite is first transformed into martensite but that the resulting martensite is so readily and quickly converted into troostite that its short existence easily escapes

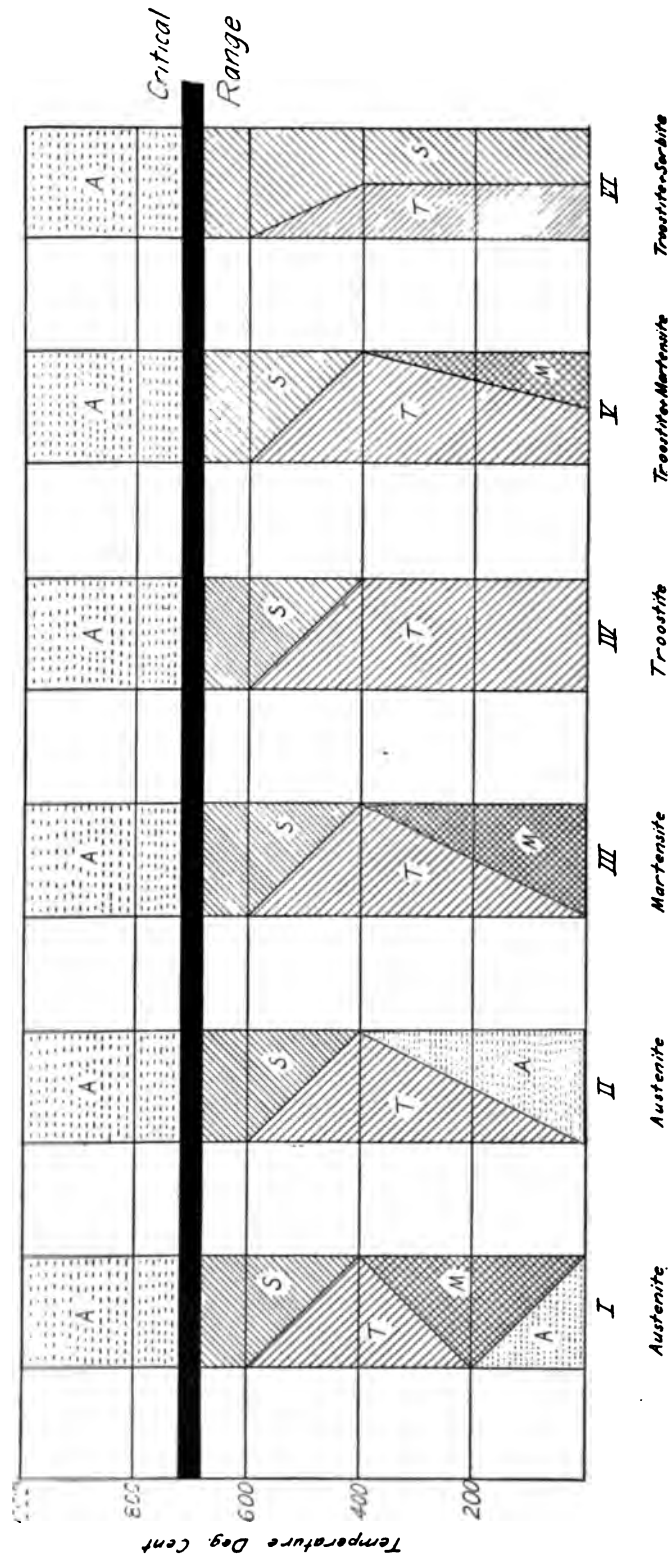


Diagram depicting the tempering of Hardened Steel

Fig. 1.

observation. His belief is based upon the following considerations: (1) the austenite retained in high carbon steel by very sudden cooling is subjected to great pressure caused by the accompanying martensite having been formed with considerable dilatation, (2) on reheating this martenso-austenitic steel the martensite is first converted into troostite, because this transformation taking place with contraction is readily induced, (3) once this transformation started, the pressure upon the austenite is released and this constituent, in turn, passes first to the martensitic stage (with increase of volume) and then quickly to the troostitic stage (with decrease of volume) the martensitic condition being of so short duration as to readily escape detection.

Tempering Martensitic Steel. — It has been shown that martensite is generally present in commercially hardened steel. Since this constituent represents a partial transformation of austenite it follows that it must be more stable than austenite at atmospheric temperature. It is sufficiently unstable, however, to be readily converted first into troostite and then into sorbite on tempering as indicated in III, Figure 1. At 400 deg. the transformation of martensite into troostite is complete, while at 600 deg. troostite is replaced by sorbite. Bearing in mind the physical properties of martensite, troostite, and sorbite, it will be readily understood why, on tempering martensitic steel, its hardness gradually decreases while it becomes less brittle and indeed quite ductile if made sorbitic.

Tempering Troostitic Steel. — Commercially hardened steel frequently contains large proportions of troostite. The tempering of troostite is depicted in IV, Figure 1. This constituent being decidedly less unstable than martensite requires greater plasticity, i.e. a higher temperature, before being transformed into a still more stable condition. Experimental evidences seem to show that the tempering of troostite, i.e. its transformation into sorbite, requires a temperature of at least 400 deg. and that at 600 deg. the transformation is complete. Since in practise the tempering of steel is seldom carried above 300 deg. it would seem as if steels made up of troostite do not need to be tempered, being sufficiently tough. There seems to be no reason to doubt the accuracy of the above inference. Commercially hardened steels, however, are generally either entirely martensitic or, more frequently, partly martensitic and partly troostitic and are in need of tempering because of the large proportion of the excessively hard and brittle martensite they usually contain.

Tempering Troosto-Martensitic Steel. — In V, Figure 1, the tempering of hardened steel containing both martensite and troostite has been depicted. It is assumed that the martensite present begins to be converted into troostite as soon as the temperature of the metal rises, while the transformation of the troostite into sorbite begins only at 400 deg.

Tempering Troosto-Sorbitic Steel. — From the diagram used to illustrate the tempering of steel it will be apparent that sorbite is relatively so stable a constituent that its transformation into pearlite cannot be effected below the critical range or, in other words, that it cannot be tempered. Indeed sorbitic steels not being hardened steels need not be considered in connection with the tempering operation. A graphical representation of the tempering of troosto-sorbitic steel, however, has been included in Figure 1. It shows that such steel remains unchanged until its temperature reaches 400 deg. when the troostite it contains begins to be transformed into sorbite, the transformation being, as usual, complete at 600 deg.

Osmondite. — It has been shown that on tempering hardened steel it is entirely converted into troostite at about 400 deg. C. Below that temperature some martensite remains in the structure, while above it some sorbite is present. To the condition

of steel when made up wholly of troostite Heyn gives the name of "osmondite." It will be apparent that osmondite does not represent a new constituent but merely a condition assumed by the steel at a certain temperature and the wisdom of giving a specific name to that condition may well be questioned.

Troostite is more readily colored by the usual etching reagents than any other constituent of steel, from which it follows that steel made up exclusively of troostite, i.e. in the osmondite condition, must exhibit maximum coloration. Again Heyn has shown that the solubility of steel in dilute sulphuric acid increases with the amount of troostite present, being maximum in steel tempered to about 400 deg. C. From

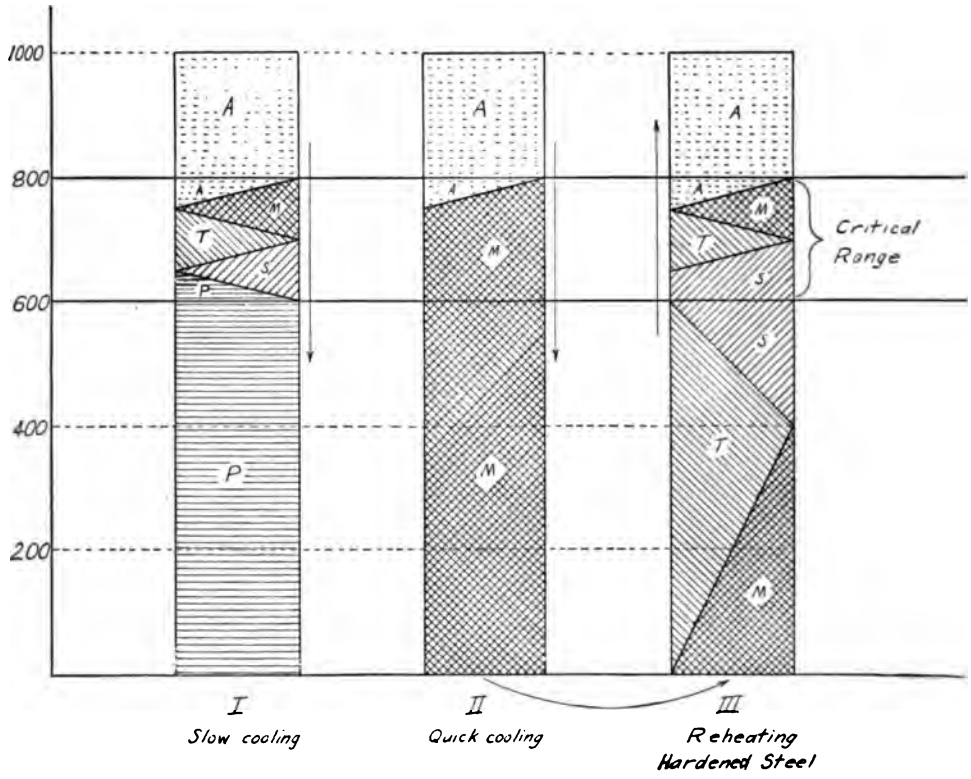


Fig. 2. — Diagram depicting the constituents formed (I) on slow cooling, (II) on quick cooling, and (III) on reheating hardened steel.

these observations Heyn described osmondite as a constituent of steel characterized by maximum solubility in acids and by maximum coloration under the action of acid metallographic reagents. In the report of the Committee on the Nomenclature of the Constituents of Iron and Steel of the International Association for Testing Materials osmondite is described as follows: "Probably aggregate. That stage in the transformation of austenite at which the solubility in dilute sulphuric acid reaches its maximum rapidity. Arbitrarily taken as the boundary between troostite and sorbite . . . The following hypotheses have been suggested, none of which has substantial experimental foundation: (1) A solid solution of carbon or an iron carbide in alpha iron; (2) The colloidal system of Benedicks in its purity, troostite being this system while forming at the expense of martensite, and sorbite being this system

coagulating and passing into pearlite; (3) The stage of maximum purity of amorphous alpha iron in the way to crystallizing into ferrite."

Structural Changes on Slow Cooling, Quick Cooling, and Reheating. — It seems helpful and instructive to depict graphically in a single diagram the structural changes taking place in eutectoid steel (1) on slow cooling through its critical range, (2) on quick cooling through that range, and (3) on reheating quickly cooled (hardened) steel above the range. The changes indicated in I (Fig. 2) show, as already explained, that steel, on cooling slowly through the critical range, is converted successively into martensite, troostite, sorbite, and pearlite. On heating the same steel from below to above the range the same changes would take place but in the reverse order. In II the steel has been cooled through the range at such speed that martensite was formed but prevented from further transformation, hardened martensitic steel being produced. The reheating of this martensitic steel is depicted in III. Below the range martensite is gradually converted first into troostite and then into sorbite. On entering the range the steel remains sorbitic but on further heating the sorbite is converted back into troostite and then into martensite. Near the top of the range austenite begins forming, the transformation being complete as the steel emerges from its range. Similar structural transformations would take place in subjecting hypo-eutectoid and hyper-eutectoid steels to like treatments, but free ferrite or free cementite would generally be present.

Microstructure of Hardened and Tempered Steel. — The structural changes corresponding to the transformations taking place on tempering hardened steel described in the foregoing pages are not always readily detected by microscopical examination. This is due to the fact that, structurally speaking, these changes are often pseudomorphic changes, the crystalline forms of the original constituent or constituents having been retained, although the nature of the crystals themselves has been altered.

Referring to pseudomorphism Dana writes, "The crystalline forms under which a species occur are sometimes those of another species." Bayley defines pseudomorphs as bodies possessing forms borrowed from another substance, or as a body possessing the form of one substance and the chemical and physical properties of another. In the formation of a pseudomorph the material of the original substance is replaced by the new substance but its external form remains unchanged.

According to Heyn the following appearances are observed in the case of eutectoid steel:

(1) After hardening but before tempering: martensite with well-developed needles remaining uncolored after an immersion of ten minutes in a solution of one per cent of hydrochloric acid in alcohol.

(2) After tempering between 100 and 200 deg.: martensitic structure unchanged but colored yellow or brown.

(3) After tempering to 275 deg.: the needle structure becomes coarser and recalls mixtures of austenite and martensite, one of the constituents remaining uncolored, the other assuming a dark coloration.

(4) After tempering to 405 deg.: the needles have disappeared and the sample appears dark and mottled suggesting a mixture of two relatively dark constituents; this is troostite.

(5) After tempering to 500 deg.: the light areas become more abundant.

(6) After tempering to 600 deg.: irregular meshes are observed rounded and light, partially surrounded by a darker network which appear to stand in relief.

Photomicrographs of the structure of hardened and tempered steels are reproduced in Figures 3 and 4. The structure of hardened steel reheated to 600 deg. has been shown in Figure 13, Lesson XII.

Carbon Condition in Tempered Steel. — It is generally admitted that the combined carbon present in steel may exist under two different conditions, (1) as hardening carbon, that is, as carbon or the carbide Fe_3C *dissolved* in iron, and (2) as cement carbon, that is, as the *crystallized* carbide Fe_3C or cementite. It is further believed (*a*) that pearlite is quite, if not altogether, free from hardening carbon, (*b*) that martensite contains, for a given steel, the maximum amount of hardening carbon that can be produced and retained in that steel by the ordinary hardening operation, and

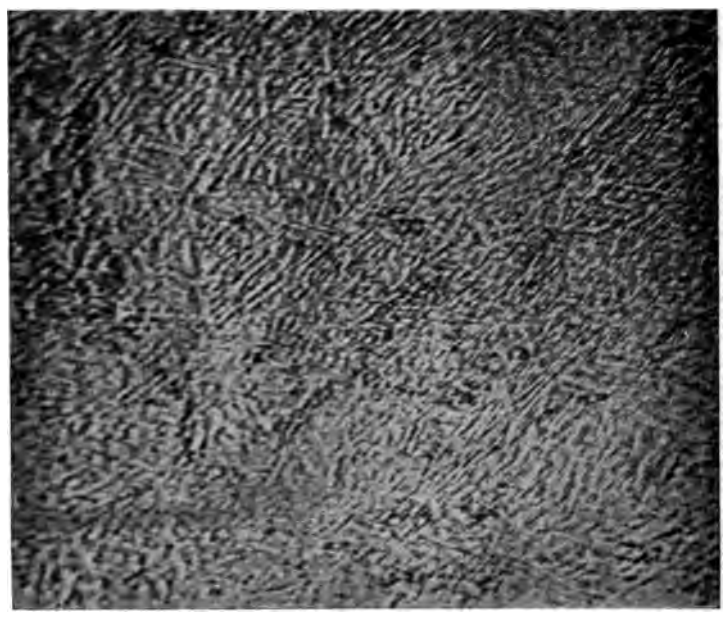


Fig. 3. — Steel. Carbon 0.45 per cent. Magnified 1000 diameters. Heated to 825 deg. C., quenched from 720 deg., and tempered between blue and brown (275 deg.?). (Osmond.)

(*c*) that on tempering martensite the amount of hardening carbon decreases as the tempering temperature increases, while the proportion of cement carbon increases correspondingly. Heyn, however, found that on analyzing the residue remaining on dissolving, in dilute sulphuric acid, hardened eutectoid steel tempered below 400 deg. it contained no carbon in the form of the carbide Fe_3C, that is no cement carbon. For the carbon remaining in the residue and which, in his opinion, is different from cement carbon, Heyn suggested the notation Cf. Not until a temperature of 400 had been reached on tempering was cement carbon detected in the residue. Heyn infers from these observations (1) that troostite contains no cement carbon, its residual carbon being in the hypothetical Cf condition, (2) that osmondite contains the maximum amount of Cf carbon, and (3) that sorbite must be formed, that is, the steel must be tempered above 400 deg. in order to produce cement carbon. Heyn further argues that the deep coloration produced on etching hardened and tempered steel is caused by the separation of Cf carbon, being, therefore, maximum in osmondite, that is, when the steel contains nothing but troostite.

Osmond very appropriately remarks that it is not necessary in order to explain Heyn's results to admit the existence of a new form of carbon, it being quite possible that the Cf carbon of Heyn is cement carbon, that is, Fe_3C so finely divided when formed below 400 deg. that it is readily decomposed by the acid, while above 400 it becomes coarser and, therefore, resists better the action of the acid.

Decrease of Hardness on Tempering. — According to Boynton the decrease of hardness taking place on tempering is gradual up to 350 deg., quite sudden between 350 and 550, and nil above 550 deg.

Heyn found the following values for the loss of hardness on tempering expressed in per cent of the original increase produced by the hardening operation:

at 100 deg.	2.5 per cent	at 400 deg.	70.0 per cent
" 200 "	14.0 " "	" 500 "	87.5 " "
" 300 "	41.0 " "	" 600 "	97.5 " "

Heyn also observed that the loss of hardness takes place most quickly at 300 deg.

Fig. 4. — Steel. Carbon 0.50 per cent. Magnified 500 diameters. Heated to 850 deg. C., quenched in water, reheated to 400 deg., and quenched in water. (W. H. Knight in the author's laboratory.)

Heat Liberated on Tempering. — In hardening steel the cooling through and below its critical range is so rapid that the transformation of austenite which would have taken place had time been given can proceed but partially, namely, to the martensitic or troosto-martensitic stage. The heat which would have been generated had the transformation been complete remains latent in hardened steel. On tempering, however, the partially suppressed transformation is permitted to proceed farther, this return to a more stable condition being accompanied by some evolution of heat. According to Osmond this latent heat can be made apparent by dissolving hardened steel in double chloride of ammonium and copper when it evolves more heat than unhardened steel.

Heyn made some careful determinations of the heat generated on tempering hardened steel. The greater acceleration in heating hardened steel was made apparent

by the differential method, using as neutral bodies similar steels in their pearlitic, that is unhardened, condition. It was observed that the heat generated on tempering is maximum at 360 deg.

Experiments

A bar of steel 6 inches long and about ½ inch square or round, preferably of eutectoid composition, should be heated well above its critical range and quenched in cold water. It should then be freed from scale and brightened by rubbing it with emery-paper, and one end of it heated in the flame of a bunsen burner. At some distance from the heated end the tempering colors will be observed in their usual order.

Pieces should now be detached from the treated bar corresponding to several tempering colors, for instance, yellow, brown, and blue, as well as a piece near the cold end and therefore not tempered. These should be polished, etched, and microscopically examined. In polishing hardened steel great care must be taken to prevent the heating of the samples, since this would necessarily cause a certain amount of tempering and therefore of structural transformation. A liberal supply of water should be used.

Two small pieces of the same steel should be hardened and reheated, one to 400 deg. C. and the other to 600 deg. The first sample should contain a great deal of troostite, the last should be sorbitic.

All samples should be photographed.

Examination

Describe the tempering (1) of martensitic steel, (2) of troostitic steel, and (3) of troosto-martensitic steel.

LESSON XV

THEORIES OF THE HARDENING OF STEEL

Many theories have been put forward to explain the hardening of steel through sudden cooling from a high temperature. They may be divided into two classes, (I) the "retention" theories and (II) the stress theory. The retention theories include (*A*) the solution theories and (*B*) the carbon theories. Three solution theories at least have been proposed, (*a*) the gamma iron theory, (*b*) the beta iron theory, and (*c*) the alpha iron theory, while two carbon theories should be mentioned, (*a*) the hardening carbon theory and (*b*) the subcarbide theory. This classification of the hardening theories is given below in a tabular form, as well as the names of their proposers and of some well-known scientists supporting them.

(I) Retention theories	(*A*) Solution theories	(*a*) Gamma Iron theory	Edwards
		(*b*) Beta iron or allotropic theory	Osmond, Roberts-Austen, Howe, and a majority of writers
		(*c*) Alpha iron theory	Le Chatelier, Guillet
	(*B*) Carbon theories	(*a*) Hardening carbon theory	
		(*b*) Subcarbide theory	Arnold
(II) Stress theory		André Le Chatelier	
		Charpy, Grenet	

Retention Theories. — The retention theories claim that in hardening steel a condition or set of conditions existing normally above its critical range is retained unchanged in the cold or but partially changed because of the rapid cooling through and below the critical range. In other words, such very quick cooling through the range denies the necessary time for the transformations to take place, at least fully, and a condition is preserved in the cold which is stable only above or within the critical range. According to these theories hardened steel, therefore, is in an unstable condition, hence the possibility of tempering it. That the transformations which would have taken place on slow cooling through the range are suppressed, partly at least, in hardening is made evident by the absence of critical points during very rapid cooling or by the appearance of feeble points only at greatly lowered temperatures. Other evidences of the partial suppression of the transformations are afforded (1) by the

condition of the carbon in hardened steel which is different from the condition of that element in unhardened steel, (2) by the evolution of heat taking place on tempering hardened steel as explained in Lesson XIV, and (3) by the structure of hardened steel.

To assume that hardened steel owes its hardness to the suppression, partial at least, of the transformations taking place on slow cooling through the critical range is, therefore, both natural and logical.

When we come to look into the nature of the constituents stable above or within the range, which on being retained in the cold impart extreme hardness to steel, we find very great differences of opinion among competent authorities.

Solution Theories. — The majority of writers believe that hardened steel is in the condition of a solid solution, quick cooling through the range having prevented the formation of the ferrite-cementite aggregate. This is strongly supported by microscopical and other evidences. They all agree that the solution consists of carbon dissolved in iron but different views are held in regard to the condition of the carbon and of the iron. While it is now the general belief that the carbide Fe_3C rather than elementary carbon is dissolved in iron, some think that in hardened steel the iron is chiefly present as gamma iron, others that it is present chiefly as beta iron, while others still believe that it exists mainly in the alpha condition. These three contentions will be briefly considered.

Gamma Iron Theory. — Edwards claims that on rapid cooling through the range iron is retained in the gamma condition. In other words that martensite, the usual constituent of hardened steel, is identical in composition if not in structure to austenite, the solid solution of carbon in gamma iron stable above the range. His contention is based solely upon the absence of the point A_2 in medium high and in high carbon steel from which he argues that beta iron does not form in these steels, dismissing the very reasonable possibility of beta iron forming at the points $A_{3.2}$ and $A_{3.2.1}$. Edwards' theory does not explain, at least satisfactorily, the marked difference of hardness between austenite and martensite nor their totally different structure. Benedicks, moreover, has shown quite conclusively that austenite cannot exist in the cold unless subjected to very great pressure, as explained in Lesson XIII. Razor blades, for instance, although made extremely hard by quenching cannot be austenitic.

Beta Iron or Allotropic Theory. — This theory put forward with great vigor and brilliancy by Osmond, championed first by the late Roberts-Austen and later by Howe and many other eminent metallurgists, contends that in hardened steel iron is present chiefly in the beta condition. It is often referred to as the allotropic theory of the hardening of steel. It should be borne in mind, however, that Osmond's allotropic theory of iron and his allotropic theory of the hardening of steel are two different conceptions. One may believe in the former without being an adherent of the latter. The allotropic theory of iron claims that iron exists in at least two and probably in three allotropic forms. No one doubts the allotropy of iron although some writers, notably Le Chatelier, believe that only two allotropic forms, namely gamma and alpha iron, have been shown to exist. The allotropic theory of the hardening of steel claims (1) that in hardened steel carbon, or more probably the carbide Fe_3C, is in solution chiefly in beta iron, hence its hardness, beta iron being very hard, (2) that hardened steel contains alpha iron, hence its magnetism, alpha iron being the only allotropic form under which iron is magnetic.

While the allotropists regard the retention of beta iron as the chief cause of the hardening of steel, they do not ignore the very important part played by carbon. They realize that the presence of carbon is essential to the retention of iron in its hard allotropic form, for in the absence of carbon it is not possible to harden iron. It is customary to compare this action of carbon in preventing the transformations to that of a brake, the more carbon the more powerful the brake action, hence the harder the steel because of the retention of a larger quantity of beta iron. They believe, however, that the hardness of quenched steel increases with the proportion of the beta iron it contains rather than with the proportion of carbon. In other words, that if it were possible to retain the same amount of beta iron with less carbon or even in the complete absence of carbon the metal would be equally hard. The allotropists do not claim that steels hardened in the ordinary way, that is, martensitic steels, are absolutely free from gamma iron. Evidences are lacking to settle this point. Again the allotropists do not deny that the internal pressure created by the transformation of austenite into the more bulky martensite may contribute to the hardness of the metal.

Summing up, in the light of this theory, the hardening of steel by rapid cooling is thus explained: (1) the bulk of the iron passes from the gamma to the beta condition, hence the great hardness produced, (2) some of the beta iron is further transformed into alpha iron, hence the magnetism of hardened steel, (3) a large proportion of the carbon or more probably of the carbide Fe_3C remains dissolved in the beta iron, the presence of this dissolved (hardening) carbon in hardened steel being proven by chemical analysis, (4) the internal pressure created by the transformation of austenite into martensite, that is, of gamma into beta iron, may contribute to the final hardness. Osmond's theory of the hardening is, therefore, based on the belief (1) in the existence of beta iron and (2) in the hardness of beta iron. Although the very existence of beta iron has been challenged by Le Chatelier and Guillet the author believes that the evidences at hand point strongly to its reality, while direct evidences of its hardness have been obtained. Rosenhain and Humfrey on straining polished bands of pure iron heated in vacuum obtained three sharply distinct structures, each one possessing different mechanical properties, especially as to hardness, and each structure representing the condition of the iron, respectively, above A_3, between A_3 and A_2, and below A_2, that is, the structure of gamma, beta, and alpha iron. The iron when in the beta condition was found to be decidedly harder than either gamma or alpha iron. These experiments point, therefore, both to the existence of beta iron and to its hardness.

On tempering hardened steel Heyn found that 70 per cent of the increased hardness produced by the hardening operation were lost in tempering below 400 deg., the remaining 30 per cent being possibly due, according to Osmond, to the internal pressure already alluded to. He further observed that hardening (dissolved) carbon did not begin to be converted into cement carbon (crystallized Fe_3C) until a temperature of 400 deg. was reached. Steel then loses most of its hardness while its carbon remains in the hardening condition. From this coexistence of softness and hardening carbon it logically follows that steel does not owe its hardness to the presence of hardening carbon, and that the presence of allotropic beta iron remains the only possible explanation. This conclusion is further supported by the fact that on tempering steel it is chiefly below 400 deg. that heat is liberated and this liberation must necessarily be ascribed to the iron returning from the beta to the alpha condition.

Alpha Iron Theory. — Le Chatelier and Guillet believe that on quick cooling through the critical range the allotropic transformation of iron from its gamma to its alpha condition is not prevented but that the steel remains, nevertheless, in the condition of a solid solution, hardened steel in their opinion being a solid solution of carbon (or of the carbide Fe_3C) in alpha iron owing its hardness to its state of solution and its magnetism to the presence of alpha iron. This view is based chiefly upon these writers' belief that the point A_2 is not an allotropic point and that therefore beta iron does not exist. The most serious objection to this theory lies in the conclusive nature of the evidences pointing to the allotropic character of the point A_2.

Carbon Theories. — The carbon theories contend that the hardness of rapidly cooled steel is due primarily to the retention in the cold of a very hard condition of the carbon normally stable only above the range, the allotropic transformation of iron playing no, or but an unimportant, part in the phenomenon. As supporting their claims they point to the fact that carbonless iron cannot be hardened and that the more carbon present the greater the increased hardness produced by quick cooling, at least up to the eutectoid carbon ratio.

These theories differ in regard to the exact condition of the carbon thus retained by quenching and imparting great hardness to the metal. The hardening carbon theory and the subcarbide theory should be briefly described.

The Hardening Carbon Theory. — It was held for many years by the majority of writers that hardened steel owed its hardness to the presence of hardening carbon, a form of carbon stable only above the range but which could be retained, in part at least, by quick cooling. This belief rested on the apparent difference existing between the condition of the carbon in hardened and in unhardened steels as proven by dissolving them in cold dilute acids when a large proportion of the carbon of hardened steel escapes as hydrocarbons, whereas nearly the totality of the carbon of unhardened steel remains as a residue which, upon being analyzed, is found to consist of the carbide Fe_3C. As to the exact nature of hardening carbon, vague, conflicting, and often extraordinary statements appeared, it being claimed by some, for instance, that hardening carbon was carbon in a diamond-like condition. It is at present believed by most that hardening carbon is carbon (or more probably the carbide Fe_3C) *dissolved* in iron, its escape as hydrocarbons upon being subjected to the action of dilute acids being due to its extremely fine state of division. If this be the nature of hardening carbon, the hardening carbon theory becomes, of course, a solution theory.

It is obvious that carbon as such, no matter how great its hardness, could not impart extreme hardness to steel in which it may be associated with 199 times its weight of soft ferrite, as, for instance, in steel containing 0.50 per cent carbon. The contention that it is not carbon, as such, which is retained by quick cooling but a very hard carbide constituting the whole or a large part of hardened steel is not, of course, open to the same objections. This is the claim of the subcarbide theory.

The Subcarbide Theory. — Arnold contends that eutectoid steel above its critical range exists as the carbide $Fe_{24}C$, a chemical compound containing about 0.89 per cent carbon. This carbide which he calls "hardenite" is very hard and being retained by quick cooling imparts hardness to quenched steel. In hypo-eutectoid steel some ferrite and in hyper-eutectoid steel some cementite are dissolved in this subcarbide. It follows from this theory that austenite and martensite correspond to different structural appearances of the same constituent, namely, the carbide $Fe_{24}C$ when of eutectoid composition, the same carbide plus ferrite or cementite in hypo- or

hyper-eutectoid steel. This theory is purely of a speculative character, the existence of the carbide $Fe_{24}C$ not being supported by a single direct evidence. It is, moreover, strongly opposed by the universally accepted theory of metallic alloys which holds that eutectic (and eutectoid) alloys immediately before their formation are not definite chemical compounds but liquid or solid solutions. On forming, whether or not it implies a change of state, the solution is transformed into an aggregate of the solute and solvent, ferrite and cementite in the case of iron-carbon alloys. The breaking up at a certain critical temperature of a definite chemical compound, as demanded by Arnold's theory, into a eutectoid aggregate of the elements of that compound is contrary to our firmly established knowledge of the mechanism of the formation of such aggregates. It implies a return to Guthrie's original error.

The Stress Theory. — In cooling steel quickly from above its critical range it is subjected to two kinds of stresses, (1) stresses due to the shrinkage of its outer shell on its interior and (2) stresses due to the transformation with increased volume of gamma into beta and alpha iron. The existence of the strains resulting from these stresses have been claimed to account satisfactorily for the hardening of steel by sudden cooling. It was argued long ago, for instance, that the hardening of steel by sudden cooling might be due to the metal being in a severely strained condition, because of the quicker cooling of the outer layers, these layers through their contraction exerting a severe pressure upon the central portion of the steel objects. The advocates of this theory pointed to the increased hardness resulting from cold working steel as a proof that severe straining produces hardness. Some went as far as to claim that cold worked steel and hardened steel are practically in the same physical condition, the quenching of steel producing, so to speak, an internal cold working (straining) of the metal. They seem to have overlooked the enormous difference between the relatively small increase of hardness produced by cold-working and the hardness resulting from quenching. In the fact that both cold-working and hardening increase the elastic limit and decrease the ductility they found additional support for their view. According to Osmond the belief once held that cold working causes an allotropic transformation is now abandoned. While it is not unreasonable to assume that the strained condition of the metal adds to its hardness it is hardly thinkable that the sudden and very great increase of hardness produced by quick cooling is due altogether to this straining. If it were so the outer layers of quenched steel implements should not be hard and razor blades could not be hardened. Again, it is impossible to reconcile this theory with the fact that it is necessary to quench steel from above its critical range in order to harden it, for one cannot conceive why, if the steel be quenched slightly below the range, the strain created in the quenching bath would be so slight as to have no hardening effect, whereas quenching from a temperature but a few degrees higher would produce very severe straining. Finally, if the contraction of the outer layers due to their rapid cooling can induce such hardening strains in the case of steel, it is surprising that a similar phenomenon is not observed in the case of other metals. The internal strains resulting from the transformation of gamma into beta iron (austenite into martensite) with increased volume afford a more acceptable explanation of the hardening of steel. It was offered long ago and has recently been revived and presented in a more scientific way, notably by André Le Chatelier, Charpy, and Grenet. It is argued that on quick cooling the allotropic transformations take place, partially at least, at a temperature so low that the metal lacks the necessary plasticity to yield to the severe stress excited by these transforma-

tions, remaining, therefore, severely strained. It becomes internally "écroui," as the French express it. Here again, however, it would seem as if the outer layers should not be strained and should, therefore, remain soft, which of course is contrary to facts. Nor is the failure of carbonless iron to harden satisfactorily explained by this theory.

Osmond believes that in hardened steel the allotropic transformations are complete, that is, that its iron exists only in the alpha condition but so severely strained (*écroui*) as to be very hard. He rests his belief chiefly on his assertion that on quick cooling the dilatation indicative of the allotropic transformations are not suppressed and that the metal does not remain non-magnetic. He overlooks the claims of the advocates of the retention theories, so strongly supported, that the transformations are not *completely* suppressed, hence the occurrence of a dilatation and of magnetism. When they are completely prevented, as in austenitic steels, the metal neither expands nor becomes magnetic on cooling.

The liberation of heat observed on tempering hardened steel points to a return to a more stable condition, supporting, therefore, the retention theories and opposing the stress theory.

Tempering and the Retention Theories. — The tempering of hardened steel, as already explained, is readily accounted for by the retention theories on the ground that the metal being in an unstable condition is ever eager to assume a more stable form, implying a return, partial at least, of the iron to the alpha condition and of the carbon to the cement condition. On heating the steel but slightly above atmospheric temperature its rigidity is sufficiently diminished to permit a slight transformation of this kind, the higher the temperature the more pronounced of course being its tempering.

Tempering and the Stress Theory. — The stress theory, likewise, satisfactorily accounts for the tempering of hardened steel on the ground that upon slight reheating the internal strains are sufficiently released to produce an appreciable decrease of the specific effects of hardening, namely, decrease of hardness, of strength, of elastic limit and increased ductility.

Summary. — From the above short description of the various theories advanced to explain the hardening of steel the reader will probably gather the impression that the retention theories, especially the beta iron theory, are the most acceptable ones. It seems quite possible, however, even probable, that the various theories, while apparently antagonistic, bring each their contribution to the elucidation of the problem. Should we not believe with the allotropists that the hardness of steel is due chiefly to the retention of a large quantity of a hard allotropic variety of iron, probably beta iron, and that this iron contains in solution the hardening carbon of the carbonists, the presence of which is absolutely essential to the existence of beta iron in the cold? Should we not with the advocates of the stress theories believe in the hardening influence of the strains created on quick cooling (*a*) because of the shrinkage of the outer layers of the metal and (*b*) because of the expansion accompanying the transformation of gamma into beta iron? None of these theories alone gives a fully satisfactory explanation. Beta iron cannot be retained in the absence of carbon and if it were it is not certain that it would be intensely hard; the presence of intensely hard iron carbide as the chief cause of hardening is contrary to evidences; the allotropic condition of hardened steel does not account satisfactorily for its hardness; the contention that quickly cooled steel is hard although its iron is in the beta condition because of its being in a state of solution is opposed by

the evidences at hand (*a*) of the existence of beta iron and (*b*) of the hardness of beta iron; Arnold's theory that hardened steel owes its hardness to the retention of a hard subcarbide of iron lacks experimental support and is scientifically untenable.

Examination

Describe briefly the various theories of the hardening of steel indicating your preference and your arguments supporting it.

LESSON XVI

THE CEMENTATION AND CASE HARDENING OF STEEL

The affinity of iron for carbon is so great that when heated to a sufficiently high temperature in contact with some suitable carbonaceous matter it readily absorbs carbon. If the heating be protracted (several days) and the amount of carbon absorbed considerable, the operation is known as "cementation" and the resulting metal as "cemented," "converted," or "blister" steel, or in Sheffield, England, as "blister bar," while if the treatment be of relatively short duration (a few hours) and the absorption of carbon in consequence superficial, it is called "case hardening."

Cementation is generally applied to wrought-iron bars which are afterwards melted (crucible process) and shaped into finished articles by casting or forging, while case hardening is applied directly to finished objects generally of low carbon steel. The purpose of cementation is to introduce carbon into wrought iron, thereby converting it into steel, the subsequent treatments (melting, forging) producing a uniform distribution of the carbon, whereas the purpose of case hardening is to manufacture steel objects with hard skins or cases while retaining their soft and tough centers or cores.

The quantity of carbon thus absorbed by iron at a high temperature but below its melting-point depends chiefly upon (1) the composition of the iron or steel subjected to carburizing, (2) the carburizing temperature, (3) the length of time at that temperature, and (4) the nature of the carburizing material.

Composition of the Iron or Steel Subjected to Carburizing. — It is probably true that the smaller the proportion of carbon in the iron the more eagerly will it take up carbon, from which it follows that as the carburizing proceeds, that is, as the metal becomes more highly carburized, additional introduction of carbon requires progressively longer time, the metal acting in this way not unlike a solution approaching its saturation point.

In the cementation process bars of very pure wrought iron and in "case hardening" steel objects containing at the most 0.20 per cent carbon are subjected to the carburizing treatment. The steel should not contain over 0.25 per cent of manganese lest the case be too brittle. The presence of certain elements appear to hinder the carburizing operation while others facilitate it.

According to Guillet the absorption of carbon is favored by those special elements which exist as double carbides such as manganese, tungsten, chromium, molybdenum, and opposed by those which form solid solutions with iron such as nickel, silicon, and aluminum.

Carburizing Temperature. — While it has been claimed that iron below its critical range will absorb some carbon this absorption, if taking place at all, is very slow, from which it is logical to infer that alpha iron has very little, if any, dissolving power for carbon. In order to produce quick and intense carburization the iron should be in its beta or, more probably, in its gamma condition, and steel, therefore, in the condi-

tion of a solid solution. Cementing and case hardening operations must consequently be conducted above the critical range of the iron or low carbon steel treated, that is, at a temperature exceeding 800 deg. C. It is also certain that the higher the temperature the quicker will carbon be absorbed and the deeper will it penetrate into the steel, that is, the deeper the "case." At Sheffield, England, where the cementation process is used more extensively than anywhere else the carburizing temperature is in the vicinity of 950 to 1000 deg. Most case hardening treatments are probably conducted in the vicinity of 900 to 950 deg. C.

Time at Carburizing Temperature. — The amount of carbon absorbed, and therefore the thickness of the case as well, increases, of course, with the length of the operation but, as already mentioned, carburization takes place more and more slowly as the carbon content increases. The maximum amount of carbon which iron can take up while in the solid state is probably not far from 2.50 per cent, this, however,

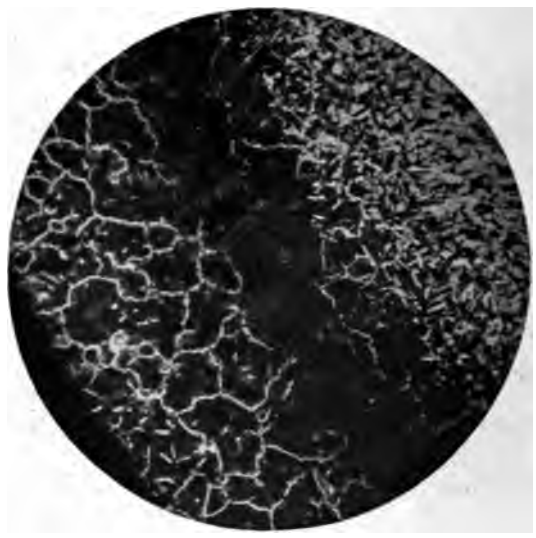


Fig. 1. — Steel. Case hardened. Magnified 20 diameters.

requiring a protracted treatment at a very high temperature. While in the manufacture of blister steel considerably more than one per cent of carbon is frequently introduced into the wrought-iron bars, in carburizing finished steel articles it is seldom desired to produce a case containing more than one per cent of carbon near the outside, a superficial, carburized layer of eutectoid composition (0.85 per cent C.) being generally considered to yield the best results. The length of time needed to produce the desired degree of carburization and desired depth of case must necessarily depend upon the nature of the metal, the kind of carburizing material used, and the temperature.

Distribution of the Carbon. — It will be apparent from the nature of the operation that in this carburizing of solid iron carbon travels slowly from the outside towards the center and that, therefore, the proportion of carbon absorbed must decrease from outside to center, unless indeed the objects treated are very thin or the treatment so long and conducted at so high a temperature as to cause even the center to absorb the maximum amount of carbon. The decrease of carbon as one approaches the core of the object is well illustrated in Figures 1 and 2. A band of hyper-eutectoid steel characterized by the presence of free cementite is frequently

d (Fig. 1) followed by a band of eutectoid composition characterized by the nce of both free cementite and free ferrite and this in turn is followed by a l showing abrupt and rapid decrease of carbon characterized by an increasing unt of free ferrite.

In case hardening operations the penetration of the carbon may be very slight ed, not exceeding 0.5 mm., while it may measure as much as 5 mm. In the ority of instances the penetration does not exceed 2 mm. This depth of penetion or thickness of case must be regulated according to requirements. It will end upon temperature, time, composition of steel, and kind of carburizing material. e mentions 0.87 mm. per hour as an average speed of penetration. As already ed, it is not generally advisable to produce a case containing more than some per cent carbon.

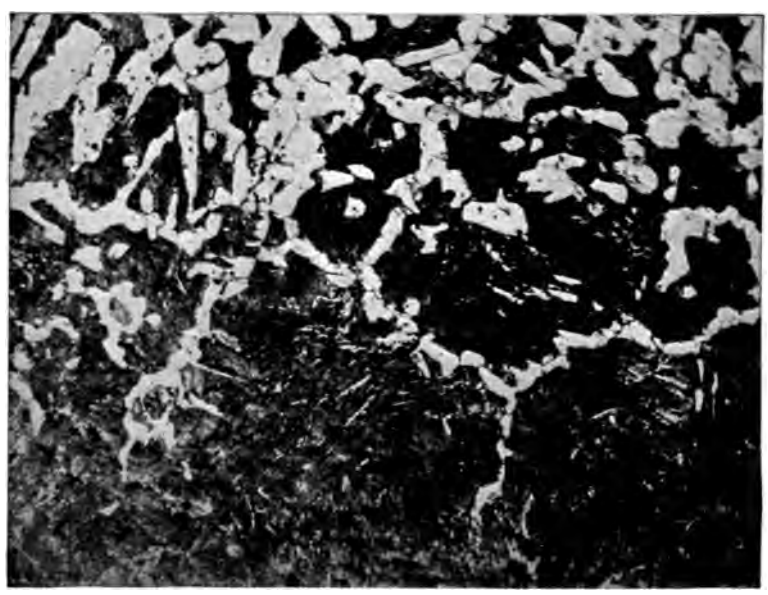


Fig. 2. — Steel. Case hardened. Magnified 100 diameters. (G. A. Reinhardt in the author's laboratory.)

The production of a deep case, while at the same time keeping the carbon content e outside of the case below one per cent, may be brought about by a rather long ment at a relatively low temperature, namely, some 850 deg. Some results obd by Guillet in regard to the influence of temperature and of time on the depth netration are shown graphically in Figure 3 as plotted by Bauer. The carbus material used was not stated. The full line represents relative penetrations at deg. after different lengths of time, namely, one, two, four, and six hours, while roken line represents the depths of penetration resulting from heating for eight s at different temperatures.

will be obvious that the process of case hardening can be controlled by the scopical examination of test pieces much more readily and accurately than by ical analysis.

Carburizing Materials. — A great variety of carbonaceous materials are used for ducing carbon in iron and steel in the solid state. These substances may be l, liquid, or gaseous. Solid materials are used more extensively than liquid or

Heat Treatment of Case Hardened Articles. — In order to refine the structure of the core which has been coarsened by a long exposure to a high temperature the metal should be reheated slightly above the critical range of that core and since its carbon content seldom exceeds 0.15 per cent carbon a temperature of at least 900 deg. C. should be used. Guillet recommends 1000 to 1025 deg. The finer structure thus imparted to the core will then be retained most effectively by quenching the metal in water or oil. By such treatment, however, the case, although hardened, is still relatively coarse since its quenching was effected at a temperature considerably exceeding its critical range. In order to refine it while leaving the structure of the core undisturbed the article should now be reheated slightly above the critical range of the case, that is, to some 750 or 800 deg. C., and then quenched in oil or water. By this double treatment we have hardened the case while conferring to it as well as to the core a fine structure.

Tempering Case Hardened Steel. — It has been seen that hardened high carbon steel is generally subjected to a tempering process, i.e. reheated to some 200 or 300 deg. C. in order to decrease its brittleness while losing but little hardness.

There seems to be at first sight no apparent reason why case hardened articles could not be likewise improved by suitable tempering following the hardening of the case. On second thought, however, it will be realized that since the chief purpose of tempering is to toughen the hardened steel and since case hardened articles depend for their toughness on the toughness of their cores little is to be gained by tempering them.

Experiments

A sample representing the cross section of a case hardened bar or other steel object should be polished, etched, and microscopically examined. The structures of the case and core described in the lesson should be noted.

If the bar has not been retreated after cooling from the carburizing heat it should be subjected to the two heat treatments described, namely, (1) reheating to 950 deg. C. followed by quenching in water or oil and (2) reheating to 800 deg. followed by quenching in water. A transverse section should be prepared for microscopical examination and the refining of both the core and case noted.

Photomicrographs of the various structures should be taken, for which a magnification of 50 to 100 diameters will be sufficient.

Examination

I. Describe the absorption of carbon by iron above its critical range.

II. Describe the best treatments to be applied to case hardened articles after carburizing and explain why they are needed.

LESSON XVII

SPECIAL STEELS

GENERAL CONSIDERATIONS

The steels so far considered in these lessons are the ordinary steels of commerce, at present often called "carbon" steels to distinguish them from the "special" steels of relatively recent origin but of rapidly growing importance. By special steels is meant those steels which owe their properties in a marked degree to the presence of one or more special elements whereas the properties of carbon steels depend chiefly, if not exclusively, for like treatment, upon the proportion of carbon present. Special steels containing but one special element are commonly called "ternary" steels, being considered to be made up of three constituents, namely iron, carbon, and the special element, while steels containing two special elements are called "quarternary" steels because of the presence of four constituents: iron, carbon, and the two special elements. These two classes of special steels will be considered separately.

Ternary Steels. — We are indebted to Guillet for a brilliantly conceived and vigorously developed theory of the ternary steels. Too rigorous an application of the theory, however, should not be insisted upon for there are some facts not yet satisfactorily explained by it. Its use, nevertheless, will be found an invaluable guide in directing researches dealing with the manufacture and the application of these steels.

Guillet's theory of the structure and properties of ternary steels may be briefly formulated by a few propositions. It is also represented graphically in Figure 1.

(1) On the introduction of a special element in carbon steel the latter remains at first pearlitic, but as the proportion of the special element increases, the carbon remaining constant, it becomes first martensitic and then austenitic (polyhedric), as shown graphically in Figure 1, and sometimes cementitic (carbide steel)[1] as later explained.

(2) By increasing the amount of carbon present in a special steel, the proportion of the special element being kept constant, it is generally converted from a pearlitic into a martensitic condition or, if already martensitic, into an austenitic condition.

(3) The greater the amount of carbon the smaller the proportion of the special element needed to cause a structural transformation, as for instance pearlite into martensite or martensite into austenite. This is indicated in Figure 1.

(4) The greater the amount of the special element the smaller the proportion of carbon needed to cause a structural transformation. This is also shown in Figure 1.

[1] Guillet uses the term polyhedric to designate an austenitic structure and carbide steel (*acier à carbure*) to indicate the presence of cementite (generally in special steels a double carbide of iron and the special element). It seems to the author that the terms austenitic and cementitic are preferable because they suggest unmistakably the nature of the constituents. Austenitic steels are not the only ones exhibiting a polyhedric structure; ferritic (low carbon) steels for instance are also polyhedric.

(5) No very sharp lines of demarcation are observed between the different types of structures mentioned in the preceding propositions, relatively wide ranges of composition existing, on the contrary, in which the steel may be partly pearlitic and partly martensitic or partly martensitic and partly austenitic, etc. These transition ranges are indicated by shaded areas in the diagram of Figure 1. Greater refinement in the construction of this diagram would undoubtedly lead to the introduction of a troostitic zone between the pearlite and martensite areas and possibly also of a sorbitic zone between pearlite and troostite.

To sum up, constituents may be formed during the *slow cooling* of many special steels which in carbon steels can only be produced by very rapid cooling through the

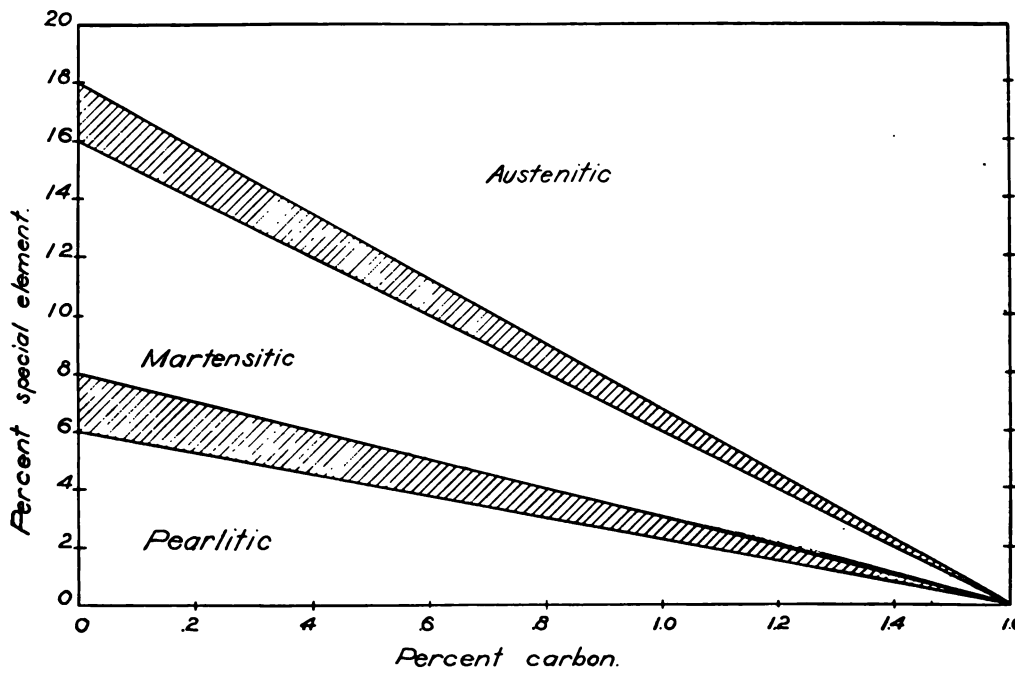


Fig. 1. — Constitutional diagram of special steels.

critical range. Carbon steels, moreover, even after very rapid cooling cannot be retained wholly in an austenitic condition while several special steels remain austenitic after slow cooling. It is evident from the above and from the diagram that in order to produce a certain structure, (1) the proportion of carbon may be kept constant while the proportion of the special element is increased until the desired structure is obtained, or (2) the proportion of the special element may be kept constant and the proportion of carbon increased, or (3) both the proportion of carbon and of the special element may be increased when the desired structure will be obtained more quickly.

The usefulness of Guillet's diagram is obvious. Should we desire, for instance, to know the kind of structure, and therefore the physical properties, of a steel containing 0.60 per cent carbon and 8 per cent of the special element, the diagram shows that such composition falls within the martensitic range. Likewise a steel containing one per cent carbon and 15 per cent of the special element would be austenitic according to the diagram. Or one may wish to know what proportion of the special element

should be added to a carbon steel containing, say, 0.5 per cent carbon, to make it martensitic; the diagram shows that 7 per cent will be needed. Again, having an austenitic steel containing 10 per cent of the special element it may be desired to know the minimum amount of carbon that may be present without causing the steel to become martensitic; the diagram shows 0.80 per cent of carbon to be the smallest proportion of carbon permissible.

The construction of such diagrams requires the preparation of a number of alloys varying in their contents of carbon and of the special element, their microscopical examination and the plotting of their structure.

It is quite essential to know the rate of cooling adopted in the construction of the diagram, i.e. whether the samples were cooled in air or more slowly in the furnace, for it is evident that their structure may be deeply affected by thus varying the speed at which they cool. Some special steels, for instance, may be pearlitic when cooled very slowly in the furnace, martensitic when cooled in air, and austenitic after water quenching.

Influence of the Special Element upon the Location of the Critical Range. — The production of martensitic and austenitic structures on slow cooling is due to the fact that the special element lowers the position of the critical point to a temperature so low (1) as to permit only a partial transformation, namely of austenite into martensite, the steel being too rigid to allow a more complete transformation, or (2) as to prevent even a slight transformation, the steel in that case remaining austenitic. This influence of the special element in lowering the position of the critical range is depicted in Figure 2 in which it is assumed that the proportion of carbon remains constant. It has been further arbitrarily assumed in this diagram that the critical point was progressively and uniformly lowered from 700 deg. C. to 0 deg., as the proportion of the special element increased from 0 to 6 per cent. From many observations it appears (1) that as long as the critical point remains above 300 deg. C. the steel becomes pearlitic on slow cooling, (2) that when the critical point is lowered below 300 deg. it becomes martensitic, the rigidity of the metal preventing further transformation, and (3) that when the critical point is lowered to atmospheric temperature or below it the metal remains untransformed, that is, austenitic. These inferences are offered here because of their apparent usefulness and suggestiveness, but the author realizes that the lines indicating the relation between the position of the critical points and the corresponding structures cannot be sharply drawn, for they are likely to shift according to the nature of the special element, the rate of cooling, etc. Again, troostitic and possibly also sorbitic steel are likely to form between pearlite and martensite, that is, whenever the critical point is lowered, say below 400 or possibly below 500 deg.

To make the meaning of the diagram of Figure 2 clear let us consider three steels: I, II, and III, all containing one per cent of carbon, but respectively 1, 4.50, and 7 per cent of the special element. As steel I cools it undergoes its transformation at about 600 deg. At that temperature the metal is so plastic that the transformation of austenite into pearlite readily takes place; the steel becomes pearlitic. The critical point of steel II is slightly below 200 deg. At this temperature the transformation of austenite into martensite will take place, but the metal is now too rigid to permit further transformations; the steel remains martensitic. Steels which remain martensitic after slow (air) cooling are said to be "self-hardening." In the case of steel III, since its critical point is lowered below atmospheric temperature it necessarily re-

mains austenitic. Since austenitic special steels have their points of transformation situated below atmospheric temperature, it should be possible through cooling to a sufficiently low temperature, as for instance by immersion in liquid air, to cause at least their partial transformation, that is, they should become martensitic after such treatment and this indeed is precisely what happens. The transformation of aus-

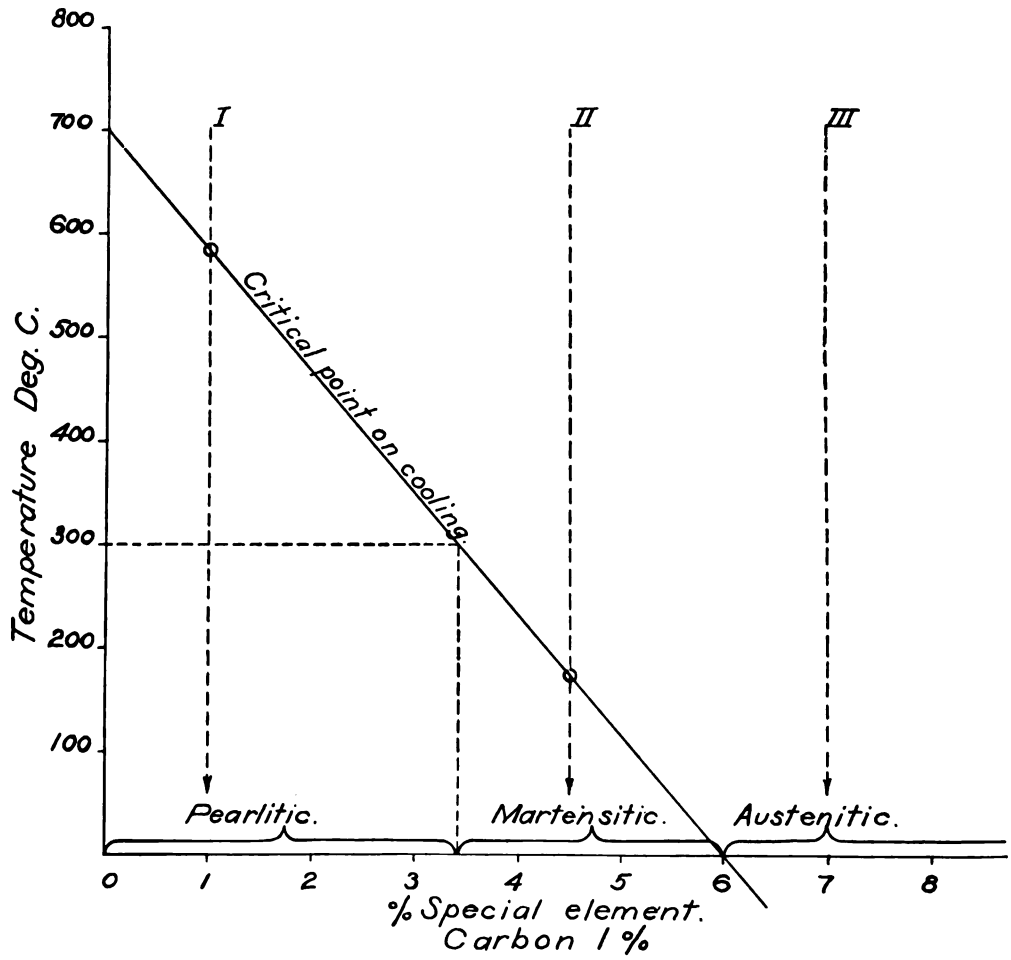


Fig. 2. — Influence of special element on the position of the critical point.

tenite into martensite takes place with increased volume and the steel from non-magnetic becomes magnetic.

In the presence of a special element lowering the critical points the influence of carbon is cumulative, i.e. the greater the proportion of carbon the more marked the action of the special element. An attempt has been made in Figure 3 to show this graphically. The diagram indicates the position of the critical point corresponding to any combination of carbon content between 0.25 and 1.50 and of the special element between 0 and 12 per cent. If the point is above 300 deg. we may assume that the steel is pearlitic, if below 300 that it is martensitic, if at or below atmospheric

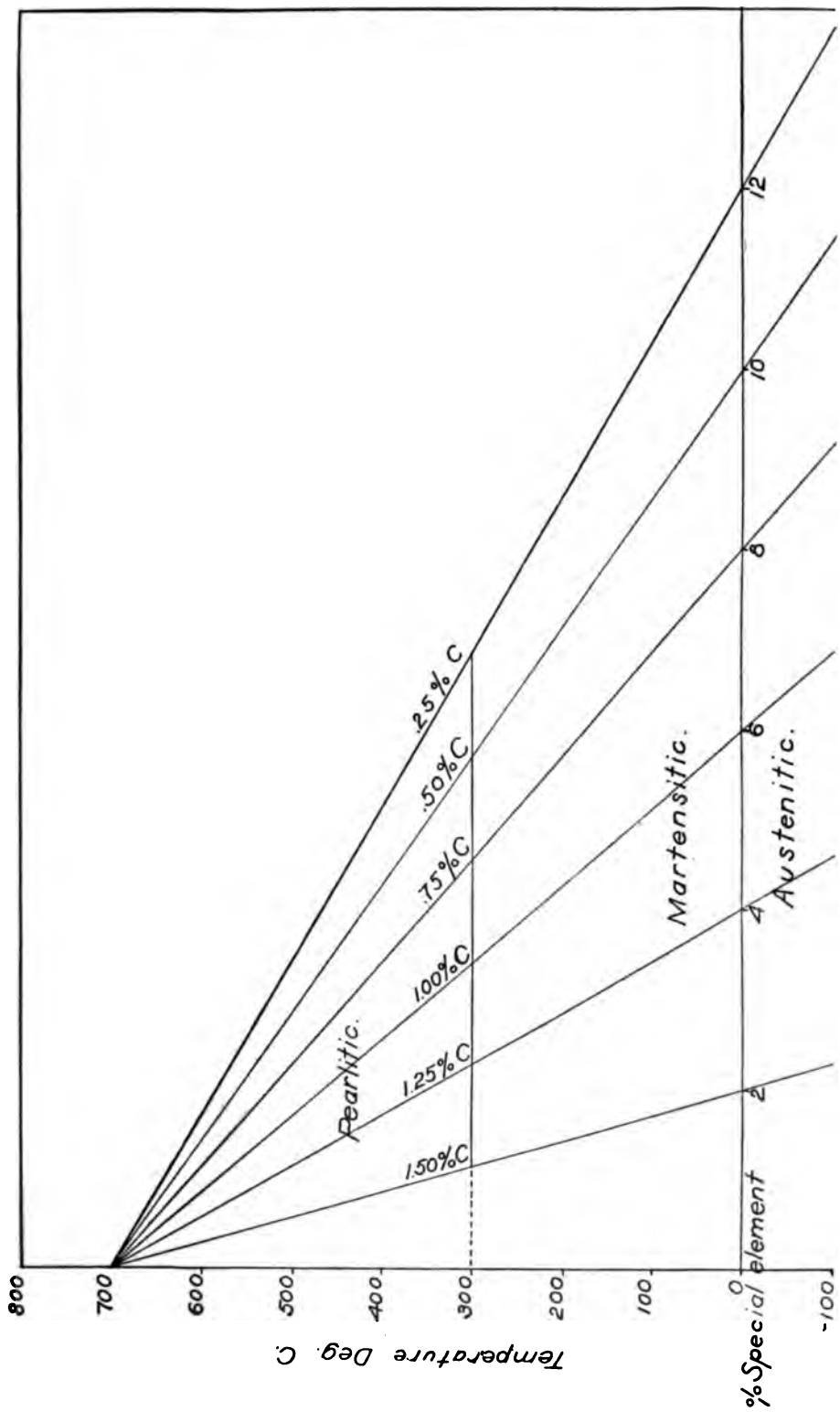


Fig. 3. — Influence of carbon and special element on the position of the critical point.

temperature that it is austenitic. In this illustration arbitrary values have been given to the combined influence of various proportions of carbon and of the special element upon the position of the critical points. The diagram shows, for instance, that while with 0.50 per cent carbon 10 per cent of the special element are required to lower the critical points to 0 deg. C., if the steel contains 1.25 per cent carbon, 4 per cent of the special element suffice. The production of pearlitic, martensitic, and austenitic structures according to the position of the critical point has also been indicated. A diagram of this kind may be even more useful than Guillet's for, while giving the same kind of information as his, it shows in addition (1) the relation between the composition of the special steel and the position of the critical point and (2) the influence of the position of the critical point upon the structure. Its construction calls for many determinations of the position of the critical point in steels of varying composition and for the microscopical examination of the corresponding structures. It is of course quite likely that as experimentally constructed it would consist of more or less smooth curves rather than of straight lines.

It will soon be shown that the influence of special elements in lowering the critical points varies greatly, from which it follows that some elements cause the production of martensitic and austenitic steels much more readily than others. Indeed some elements never cause a sufficient depression of the critical points to yield austenitic or even martensitic steels. A few elements even actually raise the location of the critical points in which case, of course, the steel always becomes pearlitic on slow cooling, regardless of its composition.

From the foregoing considerations it appears that according to their structural composition special steels may be divided into at least four classes, (1) pearlitic steels, (2) martensitic steels, (3) austenitic (polyhedric) steels, and (4) cementitic (Guillet's carbide) steels. These should now be farther considered.

Pearlitic Steels. — The pearlitic steels, as we have seen, are those which generally contain but a relatively small amount of the special element, although in case of steel very low in carbon the proportion of the special element may be quite large. In these steels the special element may (1) be dissolved in the ferrite forming with it a solid solution, (2) be combined with carbon in cementite as a double carbide of iron and the special element, or (3) be partly dissolved in ferrite and partly combined with carbon.

According to Guillet nickel and silicon, for instance, are entirely dissolved in ferrite, while manganese, chromium, tungsten, vanadium, and molybdenum are partly held in solution by ferrite and partly present in cementite as double carbides. Such terms as nickel-ferrite, silico-ferrite, mangano-ferrite, etc., have been suggested to designate ferrite holding in solution large proportions of nickel, silicon, manganese, etc., respectively.

The structure of pearlitic special steels is generally quite similar to that of pearlitic carbon steels, although the pearlite particles of special steels frequently are more angular than those of carbon steel, often exhibiting many straight sides and sharp corners, whereas the pearlite particles of carbon steel are more rounded. The lamination of pearlite is also often more minute in special steels while for same carbon content it often appears to occupy a larger bulk. From their similarity of structure, it might reasonably be inferred that pearlitic special steels should not differ much in physical properties from ordinary carbon steels. As a matter of fact, however, pearlitic special steels are often greatly superior to carbon steels generally because they possess in a much greater degree that desirable combination of properties, strength,

or rather high elastic limit, and ductility. They are also frequently harder for like ductility, and therefore better adapted to resist wear. Finally their ability to resist shocks is often markedly superior to that of carbon steels. Their uses make for greater efficiency and their greater strength permits an often welcome reduction in bulk and weight of certain parts of machinery. This greater strength and stiffness of special pearlitic steels may be due to the special element dissolving, in part at least, in the ferrite thereby increasing its strength, elastic limit, and hardness, a stronger and harder ferrite resulting in turn in a stronger and harder pearlite. The superior physical qualities of these steels may also be due, at least partly, to a finer, closer ferrite-cementite aggregate.

The critical points of special pearlitic steels generally occur at temperatures somewhat lower than those at which the critical points of carbon steel are located, this being in accord with the usual influence of special elements upon these points as already explained.

Martensitic Steels. — For the same carbon content martensitic steel contains necessarily more of the special element than pearlitic steels, while for a given proportion of the special element they must contain more carbon; they generally contain both more carbon and more of the special element than pearlitic steels. As already stated the influence of some special elements in lowering the critical points is not sufficiently pronounced to result in the formation of martensite on slow cooling. Indeed some elements raise the position of the critical points in which case pearlitic steel must necessarily always be formed on slow cooling.

The properties of martensitic special steels are not unlike the properties of martensitic carbon steels, that is of hardened carbon steel. These steels are hard and brittle and unforgeable in the cold. Their uses are very limited, chiefly because of their brittleness and of the difficulty of machining them. While resembling hardened carbon steels they are quite stable above atmospheric temperature, being little affected by tempering, i.e. by reheating to 200 or 300 deg. C. This property suggests one important application at least of martensitic special steels later to be considered, namely, their use for the manufacture of cutting tools, their greater stability permitting the tools to be heated to a higher temperature, i.e. the cutting being performed at greater speed without breaking down through excessive tempering.

The martensite of special steels probably is, like the martensite of carbon steels, chiefly a solid solution in beta iron of the carbide Fe_3C or more often of a double carbide of iron and of the special element, the magnetism of the metal being due to the presence of some alpha iron.

Austenitic (Polyhedric) Steels. — For a given carbon content austenitic steels necessarily contain more of the special element than martensitic steels, while for a given proportion of the special element they are necessarily more highly carburized. Austenitic steels generally contain both more carbon and more of the special element than martensitic steels. Their properties are as might be expected similar to those of austenitic carbon steels, that is, of high carbon steels cooled extremely quickly from a very high temperature. Austenitic steels are moderately tenacious but very ductile; they have a low elastic limit but possess a remarkable power of resisting wear by abrasion as well as rupture by shocks. Their mineralogical hardness, however, is generally inferior to that of martensitic steels.

Unlike quenched austenitic carbon steel these special steels are stable at all temperatures below their point of solidification and are not therefore greatly affected by

heat treatment unless of a protracted nature. They should be, however, free from separated carbides. If not they should be heated to a high temperature so as to cause the solution of these carbides, and then quenched to prevent their separating again.

The austenite of special steels undoubtedly consists of a solid solution in gamma iron of carbon and of the special element, probably of a double carbide. Because of the absence of alpha iron austenitic steels are non-magnetic.

Austenitic special steels find useful application for parts of machinery and the like subjected to very severe wear by abrasion and to shocks. Their low elastic limit and the difficulty of machining them are the chief reasons preventing their wider use.

Cementitic (Carbide) Steels. — Some special elements on being introduced in increasing proportions fail to convert the metal into austenite, free particles of a double carbide of iron and the special element being formed instead and embedded in a martensitic, troostitic, sorbitic, or pearlitic matrix. Guillet calls these "carbide" steels. Such elements as chromium, tungsten, molybdenum, and vanadium when present in sufficient quantity produce cementitic steels. The most valuable property of these steels is their power, when the carbides are embedded or rather dissolved in a martensitic matrix, of retaining their hardness when heated to such temperature as would readily cause the softening of hardened carbon steel, thus permitting their use in the shape of tools at such speed as to cause their cutting edges to become visibly hot. This phenomenon will be further explained when describing self-hardening and high speed steels.

Treatments of Special Steels. — Special steels are subjected to the same treatments as carbon steels, i.e. to hot and cold working, annealing, hardening and tempering, and to case hardening. Since the special elements, however, often have a marked influence on the position of the critical points it is obvious that the temperatures indicated as the most suitable ones for the annealing and hardening of carbon steels may not be satisfactory in the case of special steels. The position of the critical points should in every case be determined and the heat treatments conducted accordingly. Greater care is also frequently needed in the forging of special steels, many of them not being quite as malleable as carbon steels. Finally some of the special elements promote the absorption of carbon by iron below its solidification-point while others oppose it and these influences must be considered in case hardening special steels. The treatment of special steels will be considered further in the next lesson in connection with the description of some of the most important commercial types.

Treatment of Pearlitic Steels. — Pearlitic special steels may, like carbon steels, be subjected to annealing, hardening, tempering, and case hardening. Their critical points, however, being generally lower, the proper temperatures for these operations are likewise lower. They should be determined for each steel. According to Guillet, however, the steel should be heated quite a little above its critical range because in the case of the pearlite of special steels its transformation into a solid solution does not take place as readily. The steel should then be cooled to near its critical range before quenching. Guillet writes that pearlitic special steels may be divided into (1) those that are not very sensitive to annealing, namely nickel and silicon steels, and (2) those that are very sensitive to annealing, namely manganese, chrome, vanadium, tungsten, and molybdenum steels. It should be noted that in the first group the special elements are supposed to be entirely dissolved in the iron, while in the second group they are partly dissolved and partly present as carbides. The case hardening of pearlitic special steels may result in the production of martensitic or even austen-

itic cases without the necessity of rapid cooling from above the critical range. This will be readily understood by referring to Figure 1 where it will be seen that by keeping the proportion of the special element constant and increasing the carbon the steel may be converted from a pearlitic to a martensitic and even to an austenitic condition. The nearer the steel to the boundary between the pearlitic and martensitic zones the more readily, of course, will it become martensitic on case hardening because the smaller the amount of carbon needed to produce that transformation. This possibility of producing steel objects with a pearlitic soft core and a hard martensitic shell without quenching from a high temperature and therefore without exposing the objects to the dangers of the quenching bath does not seem to have received the attention it deserves for it suggests important practical applications. And likewise the production of a soft pearlitic core surrounded by a hard martensitic steel, itself surrounded by a tough austenitic steel. It points at least to the manufacture of pearlitic steel objects which can be readily machined, etc., and as a last treatment made austenitic to a certain depth, being in this way greatly superior to the austenitic steels at present used, which being cast in an austenitic condition can be machined only with very great difficulty.

Treatment of Martensitic Steels. — Unlike martensitic carbon steels martensitic special steels being quite stable below the critical range of the metal are not readily affected by tempering treatments. It should be borne in mind, however, that some special steels which are martensitic after air cooling may become pearlitic, in part at least, after very slow cooling in the furnace and austenitic or martenso-austenitic after quenching in water. By selecting a special steel of suitable composition, for instance, and allowing it to cool in a furnace it becomes pearlitic and can in consequence be machined; after machining the finished object may be made martensitic by cooling in air, doing away with the necessity of the quenching bath and its inherent evils. It is evident that for this purpose the composition of the steel should be near the boundary line between the pearlitic and martensitic zones. The author believes that the practical possibilities of this procedure have been overlooked. When working near the pearlito-martensitic boundary line the formation of troostite is of course always likely.

Treatment of Austenitic Steels. — Austenitic special steels are stable theoretically at least at all temperatures and should not, therefore, be affected by heat treatment of any kind. Some special steels, however, may require air cooling to be truly austenitic, in which case very slow cooling in the furnace may result in the production of some martensite or troostite and even of some pearlite, accompanied by the reappearance of magnetism. It also frequently happens that during the relatively slow cooling of austenitic steels some free cementite may be formed, consisting generally of a double carbide of iron and the special element, this setting free of cementite being generally accompanied by a decided decrease of strength and ductility. In order to cause the reabsorption of the separated carbide heating to a high temperature (1000 deg. C. or higher) is generally required followed by rapid cooling in water or oil so as to prevent its separating again on cooling. This treatment is sometimes called "water toughening."

Treatment of Cementitic Steels. — Cementitic steels contain many particles of cementite or double carbide embedded in a matrix which may be martensitic, troostitic, sorbitic, or pearlitic according to the rate of cooling. It is often desirable to cause the disappearance in part at least of these particles while producing a finely martensitic structure, and for this purpose heating to a high temperature (1000 deg.

or more) followed by relatively quick cooling is necessary. Cooling in air is often sufficiently rapid to retain the carbide in solution, as for instance in the case of the high speed steels soon to be described.

Quaternary Steels. — Quaternary steels like ternary steels may be pearlitic, martensitic, austenitic, or cementitic as well as sorbitic and troostitic. If the two special elements are present in small quantities the steels remain pearlitic. If they contain one or two cementite forming elements such as chromium, tungsten, molybdenum, etc., they are likely to be cementitic, that is, to contain many particles of a double or triple carbide. These should generally be made to dissolve in the matrix by heating to a high temperature followed by rapid cooling when a finely martensitic structure, quite free from cementite, may be produced as in the treatment of high speed steel. If the quaternary steels contain considerable proportions of two special elements capable of forming solid solutions with iron, as for instance nickel and manganese, they are frequently martensitic or austenitic. A large proportion of an element which is partly dissolved in ferrite and partly present in cementite as a double carbide, manganese, for instance, may result in the occurrence of cementite particles embedded in an austenitic matrix.

Examination

I. Describe and explain Guillet's diagram showing the structural composition of special steels corresponding to varying proportions of carbon and of the special element.

II. Explain the influence of some special elements on the position of the critical points.

III. Explain the superiority of pearlitic special steels over pearlitic carbon steels.

IV. Explain any difference which may exist between the martensite of special steels formed on slow cooling and the martensite of carbon steel produced by quick cooling.

V. Explain the possible production in the case hardening of some pearlitic special steels of martensitic or even austenitic cases without quenching.

LESSON XVIII

SPECIAL STEELS

CONSTITUTION, PROPERTIES, TREATMENT, AND USES OF MOST IMPORTANT TYPES

The present lesson is devoted to a brief consideration of the composition, structure, properties, treatments, and uses of those special steels which have been found to be of commercial value, namely, nickel, manganese, tungsten, chromium, vanadium,

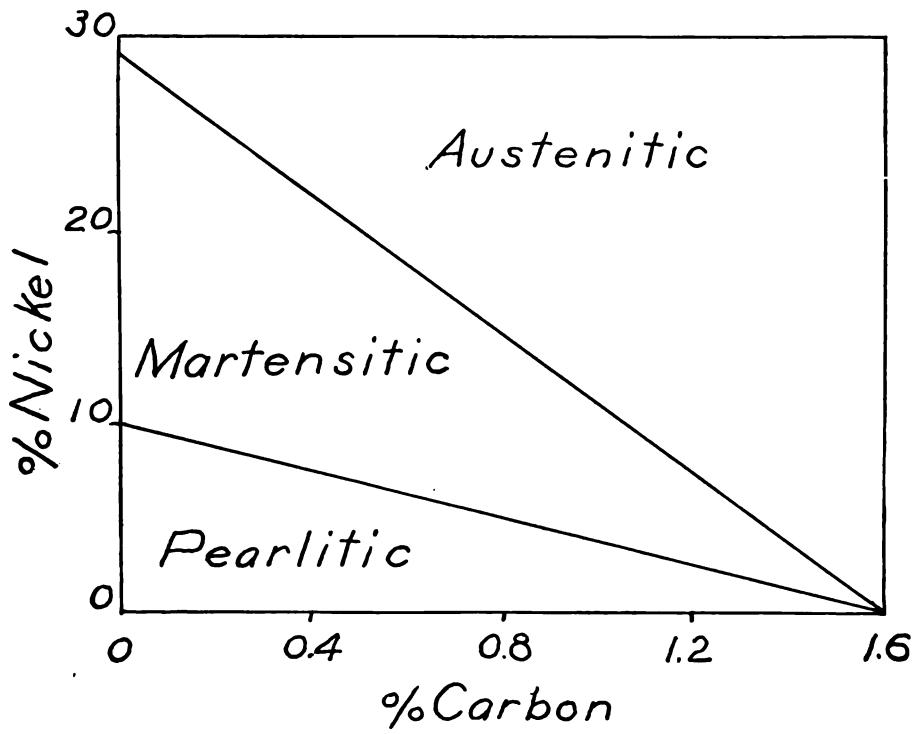


Fig. 1. — Nickel steel. Constitutional diagram. (Guillet.)

silicon, chrome-nickel, chrome-vanadium, chrome-tungsten, and chrome-molybdenum steels.

Nickel Steel. — Nickel apparently dissolves in iron in all proportions. The constitutional diagram of nickel steel is illustrated in Figure 1 after Guillet. In view of the explanation of such diagrams given in the preceding lesson it will be readily understood. It shows that as the carbon increases from 0 to 1.60 per cent and the nickel from 0 to 30 per cent the metal which at first remains pearlitic becomes martensitic

and finally austenitic. The nickel steels of greatest commercial importance seldom containing more than 5 per cent nickel and one per cent carbon are pearlitic. This influence of nickel in preventing partly or wholly the transformation of austenite into pearlite is due to its lowering the critical point of the steel as fully explained in the last lesson and as illustrated graphically in Figure 2 in the case of iron-nickel alloys containing small proportions of carbon. It should be remembered that the presence of larger quantities of carbon would intensify the influence of nickel, i.e. would cause the critical points to be further depressed. The diagram shows that as the nickel increases from 0 to some 25 per cent both transformations, AB on cooling and $A'B'$ on heating, are depressed, the former, however, much more quickly than the latter, resulting in a rapidly increasing gap between the two transformations. In other words, nickel up to 25 per cent greatly increases the hysteresis. Taking a steel, for instance, with 10 per cent nickel cooling from a high temperature, it remains non-magnetic

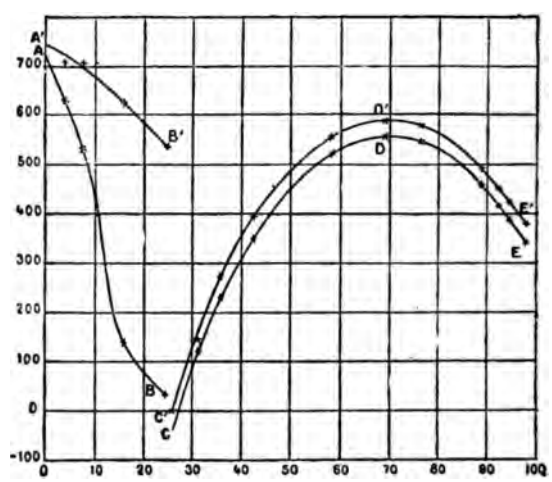


Fig. 2. — Influence of nickel on the critical points of iron. (Osmond.)

until a temperature of some 400 deg. C. is reached when it undergoes the magnetic and other transformations. On reheating this magnetic steel, however, it does not again lose its magnetism until a temperature of some 675 deg. is attained. Between 400 and 675 deg. this nickel steel will be magnetic, therefore, in case its last transformation resulted from cooling below 400 deg. and it will be non-magnetic if it resulted from heating above 675 deg. When this hysteresis gap between the transformation is considerable the alloys are said to be irreversible, meaning by that expression that the reverse transformation cannot be produced at or near the same temperature. Nickel steels containing between 0 and 25 per cent are therefore often spoken of as irreversible alloys. It should be noted, however, that when the nickel content does not exceed some 3 per cent the alloys are really reversible, that is, the gap between the critical transformations on heating and cooling is not excessive. According to Osmond, for instance, with 3.82 per cent nickel the critical point on heating occurs at 710 deg. and on cooling at 628 deg. A gap of 100 deg. might be arbitrarily selected as a line of demarcation between reversible and irreversible alloys. Returning to Figure 2 it will be seen that as the nickel content increases above 25 per cent the transformations

become abruptly reversible (the gap between them not exceeding 50 deg.), that their position is now gradually lifted, reaching a maximum for about 70 per cent nickel, and that it is then again lowered. Iron-nickel alloys containing more than 25 per cent nickel are therefore reversible.

The diagram also shows that with some 25 per cent nickel the transformation is lowered below atmospheric temperature which means that the metal on cooling from above B' remains non-magnetic at atmospheric temperature and that its iron, therefore, is in the gamma condition and its structure austenitic.

An attempt has been made in Figure 3 to construct a diagram indicating the relation existing between carbon content, nickel content, position of the critical points on cooling, and corresponding types of structure as explained in Lesson XVII.

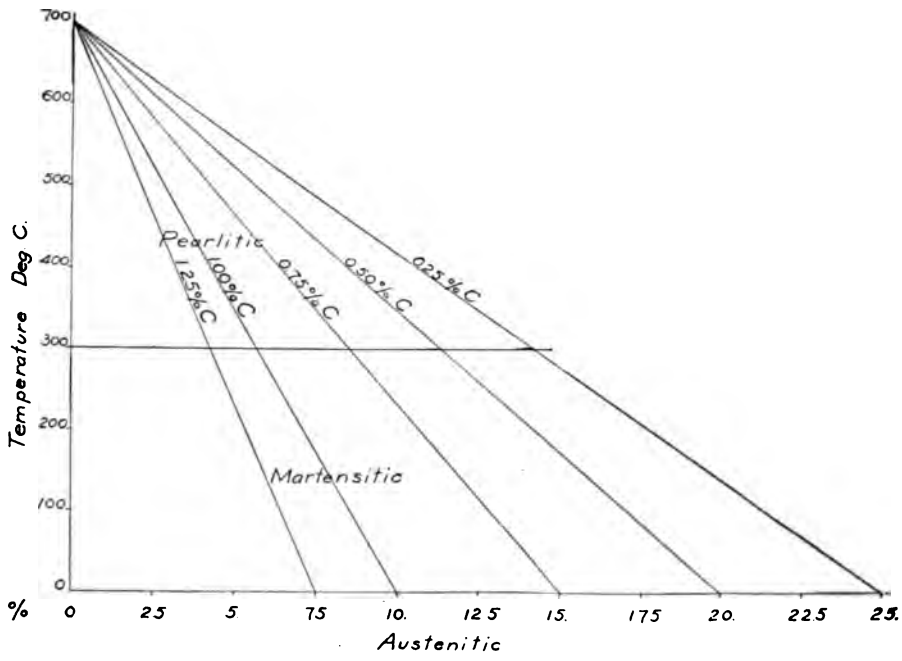


Fig. 3. — Influence of nickel and carbon on the position of the critical point Ar_1 and corresponding types of structure.

As already stated the pearlitic nickel steels are those most widely used. In the majority of cases the nickel content does not exceed 3.50 per cent while the carbon content is seldom over 0.50 per cent. These steels compared with carbon steels of equal ductility have a considerably higher strength and especially higher elastic limit, while compared with carbon steels of like elastic limit they have much greater ductility. To explain this in another way, the introduction of some 3.50 per cent nickel in a 0.50 per cent steel, for instance, raises its elastic limit very considerably while decreasing its ductility but slightly. Pearlitic nickel steels are also somewhat harder than carbon steels of like properties, hence better able to resist wear. When properly heat treated their ability to resist shocks is likewise greater.

The structure of pearlitic nickel steel is shown in Figure 4. On comparing it with that of carbon steel of like carbon content it will be noted that the pearlite particles are somewhat sharper and more angular and the ferrite grains smaller. When exam-

ined under high magnification the nickel pearlite is seldom found as distinctly laminated as ordinary pearlite.

The hardening and annealing of nickel steels should be conducted at lower temperatures than the hardening and annealing of ordinary steels of similar carbon content since their critical points occur at lower temperatures. From the evidences at hand it would seem as if between 0 and 5 per cent nickel, and in the case of low carbon steels, each one per cent of nickel lowered the Ar_1 point some 20 deg. C. and the Ac_1 point some 10 deg. In the nickel pearlitic steels of commerce, therefore, the points Ar_1 and Ac_1 should occur at or near the temperatures indicated in the following table according to their percentage of nickel.

Fig. 4. — Nickel steel. Carbon about 0.30 per cent. Nickel about 3 per cent. Magnified 100 diameters. (G. A. Reinhardt in the author's laboratory.)

% Ni	Ac_1	Ar_1
0	750	700
0.50	745	690
1.00	740	680
1.50	735	670
2.00	730	660
2.50	725	650
3.00	720	640
3.50	715	630
4.00	710	620
4.50	705	610
5.00	700	600

While nickel retards the carburization of iron by case hardening, the cores of nickel steel articles are not coarsened by the high temperature of the carburizing operation to the same extent as carbon steel cores, so that one treatment is often sufficient, namely reheating to and quenching from a temperature slightly superior to the crit-

ical range of the case, that is, to some 700 to 750 deg. in the presence of some 3 or 3.5 per cent nickel. Higher nickel contents call for lower quenching temperatures.

The case hardening of nickel steels offers the possibility already alluded to of producing a martensitic case without quenching. Nickel steel, for instance, containing not over 0.25 per cent carbon and some 3.50 or more per cent nickel can readily be made martensitic near the outside by case hardening followed by air cooling as shown in Figures 5 and 6. The martensitic grains owe their polyhedral form to the original austenitic grains from which they are derived. The thickness of the mastensitic case is about 0.5 mm. The occurrence of troostite should be noted. Under lower magnification (Fig. 6) a solid troostite band is seen to separate the martensitic and the sorbito-pearlitic portions. With a little more carbon and nickel martenso-austenitic cases may be produced as shown in Figures 7 and 8.

Nickel steels that are martensitic as cast are not utilized because like all martensitic steels they are hard, brittle, and cannot be machined. Their case hardening should result in the formation of ductile, austenitic cases. Nickel steels which are martensitic after air cooling may be troostitic, sorbitic, or even pearlitic after very slow cooling in the furnace, while they may become austenitic on water quenching. The structure of martensitic nickel steel is shown in Figure 9.

Austenitic nickel steels are not widely used, the high carbon, high manganese steels being preferred when an austenitic steel is desired, in part at least because of their lower cost. Like all austenitic steels they are non-magnetic, ductile, very difficult to machine and have a low elastic limit. Their structure is polyhedric (see Fig. 10), Some types of austenitic nickel steels have, however, found interesting applications based chiefly on the marked influence of nickel on the dilatation of the metal. With 36 per cent nickel, for instance, the dilatation is nearly nil and the resulting alloy, discovered by Guillaume, and called by him "invar" is used successfully for the construction of clocks and other instruments of precision. With some 46 per cent of nickel and 0.15 per cent carbon the coefficient of dilatation is nearly the same as that of glass and alloys of that composition called "platinite" are used in place of platinum for the construction of incandescent electric lamps. Austenitic nickel steel, like all austenitic special steels, may be made martensitic and thereby regain its magnetism by immersion in liquid air. The increase of volume which accompanies this transformation produces a swelling of the polished surface which because of the resulting relief effect renders the structure of the metal apparent without etching, as shown in Figure 11.

Manganese Steel. — Manganese, when alloyed with iron and carbon in large proportion is partly dissolved in the iron and partly present as a double carbide of iron and manganese. From this behavior of manganese the structural types formed by increasing both carbon and manganese may be anticipated. The steel should at first remain pearlitic and then become in succession martensitic and austenitic. With much manganese and carbon, however, the separation of carbide is to be expected. The constitutional diagram of manganese steels is shown in Figure 12 after Guillet, while a critical point structural diagram has been constructed tentatively in Figure 13. By comparing the constitutional diagram of manganese steel with that of nickel steel it will be noted that manganese is, roughly stated, twice as effective as nickel in producing a certain type of structure, as for instance in converting pearlitic into martensitic steel.

Manganese is present in appreciable quantities in all ordinary carbon steels but

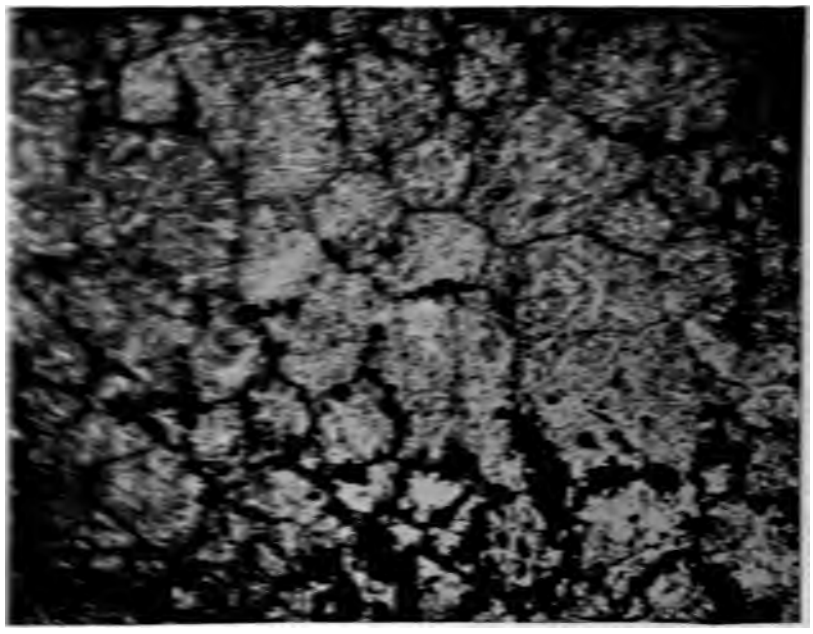


Fig. 5. — [illegible] Carbon 0.17 per cent. Case [illegible] Magnified 50 diameters. G. A. Reinhardt in [illegible]

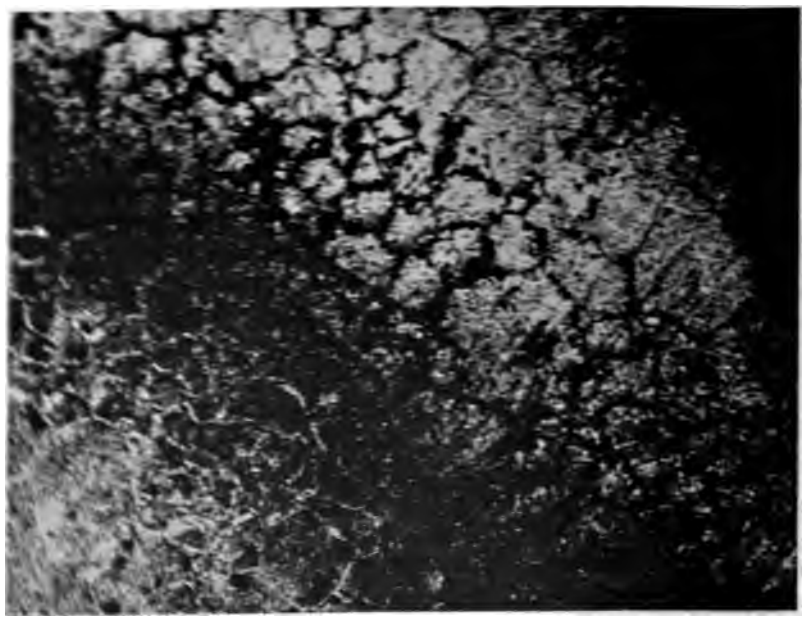


Fig. 6. — Same steel as in Fig. 5. Same treatment. Magnified 50 diameters. (G. A. Reinhardt in the author's laboratory.)

Fig. 7. — Nickel steel. Nickel 4.86 per cent. Carbon 0.115 per cent. Case hardened and air cooled. Magnified 100 diameters. (G. A. Reinhardt in the author's laboratory.)

Fig. 8. — Same steel as in Fig. 7. Same treatment. Magnified 300 diameters. (G. A. Reinhardt in the author's laboratory.)

unless the latter contain considerably more than one per cent of that element they are not regarded as manganese steels. With carbon not exceeding 0.80 per cent and manganese not exceeding some 3 per cent the steels remain pearlitic and, therefore, not unlike the pearlitic nickel steels so widely used. Manganese pearlitic steels, however,

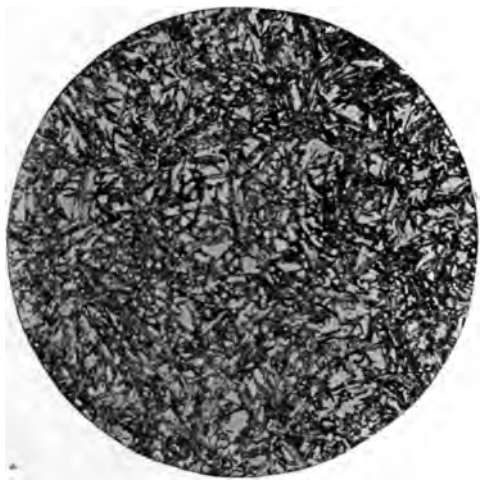


Fig. 9. — Nickel steel. Cast. Nickel 10 per cent. Carbon 0.80 per cent. Magnified 300 diameters. (Guillet.)

Fig. 10. — Nickel steel. Nickel 25 per cent. Carbon 0.80 per cent. Magnified 300 diameters. (Osmond.)

Fig. 11. — Nickel steel. Nickel 15 per cent. Carbon 0.80 per cent. Cooled in liquid air (−180 deg. C.). Not etched. Magnified 300 diameters. (Guillet.)

are practically ignored by steel manufacturers and users apparently (1) because of the wide-spread belief that such steels are brittle, and (2) because of the difficulty of manufacturing low carbon manganese steels. The belief in the brittleness of pearlitic manganese steels is founded on Hadfield's statement that between 2 and 6 per cent of manganese the steels are hopelessly brittle. On closer examination, however, it would

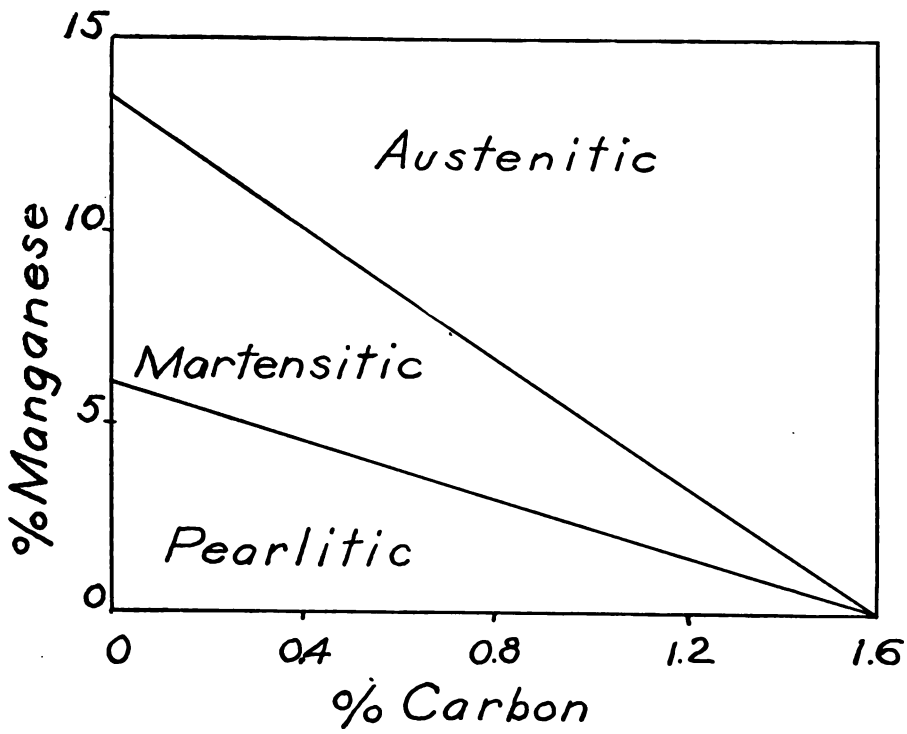


Fig. 12. — Manganese steel. Constitutional diagram. (Guillet.)

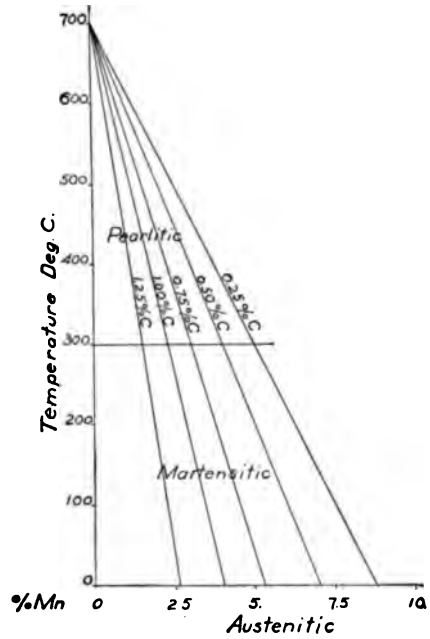


Fig. 13. — Influence of manganese and carbon on position of critical point Ar_1 and corresponding types of structure.

seem as if this statement was true only in the case of rather high carbon steels cooled relatively quickly. Evidences have since been offered, notably by Guillet, showing that *low carbon* pearlitic manganese steel *slowly cooled* is not brittle. These steels have been difficult to manufacture because of the necessity of using ferro-manganese from the blast furnace and therefore high in carbon, thereby introducing much carbon in the steel. At present, however, nearly carbonless ferro-manganese is produced in electric furnaces and also by the thermit process. It is also claimed that low carbon manganese steels can be successfully produced in the electric furnace under suitable oxidizing conditions and at high temperature when carbon may be oxidized in preference to manganese. If the physical properties of low carbon pearlitic manganese steel are at all comparable to those of pearlitic nickel steel and if manganese steel can be manufactured more cheaply than nickel steel of like properties the manufac-

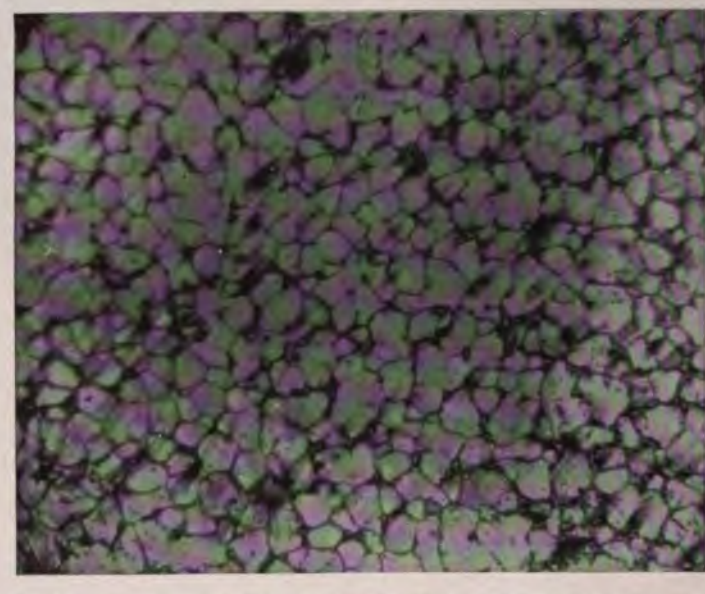


Fig. 14. — Manganese steel. Austenitic. Cast. Magnified 50 diameters.

ture and testing of low carbon manganese steel should receive more attention. The possibility of producing by case hardening articles having pearlitic cores and austenitic cases also deserves some consideration. Martensitic manganese steels are not utilized because of the hardness and brittleness which they share with all martensitic steels. Those manganese steels whose composition is near the boundary line between the pearlitic and martensitic regions while martensitic after air cooling may be troostitic or even pearlitic after very slow cooling while they may become austenitic on quenching.

Austenitic manganese steel is of considerable industrial importance. It is often called from the name of its inventor " Hadfield " steel. It generally contains from 10 to 15 per cent manganese and from one to 1.5 per cent carbon. In its cast condition it is weak and has but little ductility probably because of the presence of a considerable quantity of free carbide. On being heated to a high temperature (1000 deg. C. or more), however, and quenched in water or oil its tenacity is greatly raised and it

becomes very ductile; the treatment being often called on that account " water toughening." The marked change of properties resulting from it is probably due to the ab-

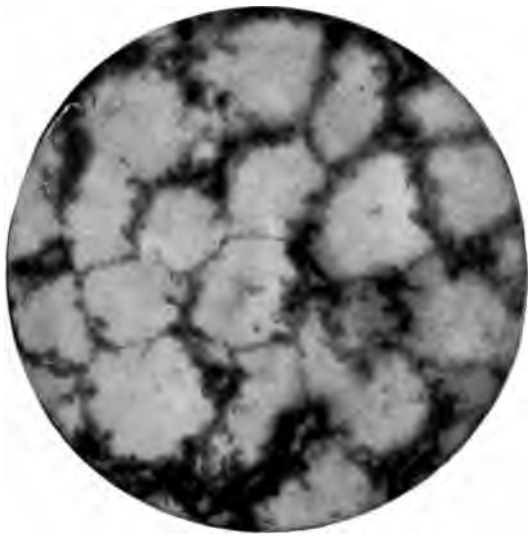


Fig. 15. — Same as in Fig. 14. Magnified 300 diameters.

sorption of the carbide at a high temperature and its retention in solution by quick cooling. The structure of manganese steel both in its cast and in its water quenched condition is shown in Figures 14 to 16. In the cast sample the carbide is seen to occur

Fig. 16. — Manganese steel. Austenitic. Water quenched. Magnified 200 diameters. (Guillet.)

as thick membranes surrounding the austenitic grains and here and there in chunks. The treated sample is nearly free from carbide and possesses the polyhedric structure characteristic of gamma iron and of austenite. The properties of austenitic man-

ganese steel are those of austenite, namely low elastic limit but great hardness and wearing power combined with much ductility.

Tungsten Steels. — Tungsten appears to raise rather than lower the critical points of iron while it forms with it a double carbide of iron and tungsten from which it may be safely inferred that tungsten steels will at first remain pearlitic on slow cooling and that as the percentage of tungsten increases it will become cementitic, that is it will contain carbide particles. This is shown in Figure 17, which is a reproduction of the constitutional diagram of tungsten steels according to Guillet. In the presence of a considerable proportion of tungsten, however, the position of the Ar_1 point

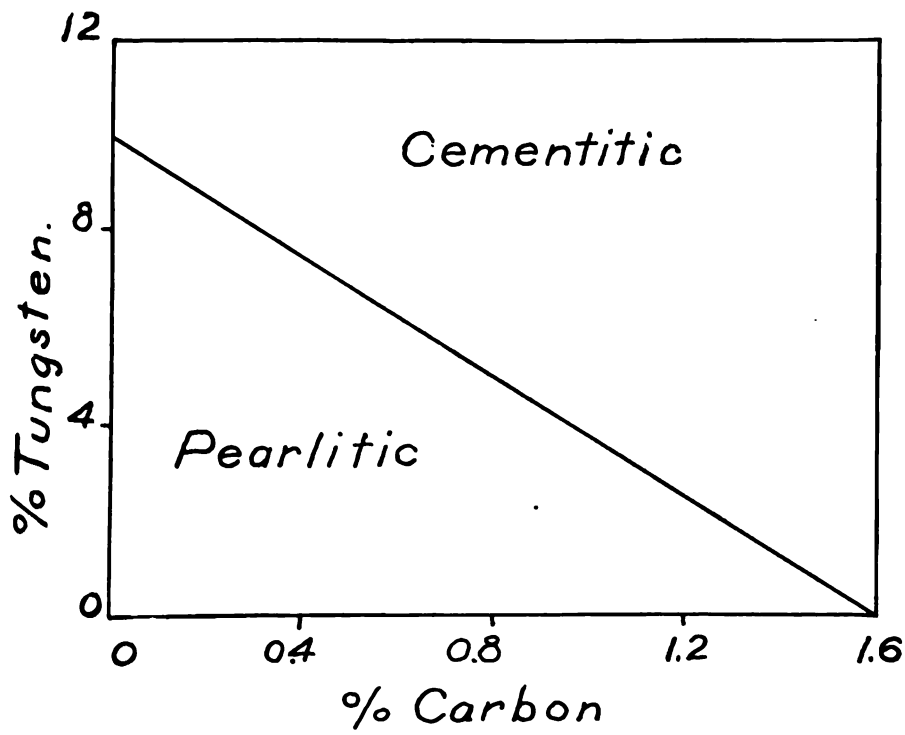


Fig. 17. Tungsten steel. Constitutional diagram. (Guillet.)

seems to be greatly affected *by the temperature from which the steel cools.* Osmond, for instance, found in the case of a steel containing 0.42 per cent carbon and 0.25 per cent tungsten that heating to and cooling from some 900 deg. reveals the existence of two critical points respectively at 690 and 650 deg. As the temperature from which cooling begins increases, however, two interesting phenomena are observed, (1) the upper point occurs at practically the same temperature but becomes fainter and finally disappears, and (2) the lower point remains pronounced but *its position is gradually lowered.* Cooling from 1015 deg., for instance, resulted in a faint critical point at 670 deg. while the lower point was depressed to 625 deg.; cooling from 1210 deg. caused the disappearance of the upper point while the lower remained very pronounced but now occurred at 500 deg. Böhler, likewise experimenting with a steel containing 0.85 per cent carbon and 7.78 per cent tungsten, reports the existence of a point at 710 deg. and one at 550 deg., the upper one, however, occurring only when

the metal has not been heated above 1100 deg. while the second is only to be detected when the temperature exceeds 1000 deg. In other words on cooling from above 1100 deg. the lower point only occurs, on cooling from below 1000 deg. only the upper point is visible, while heating to and cooling from a temperature situated between 1000 and 1100 deg. causes the appearance of both points. It will be shown soon that this indirect influence of tungsten upon the critical points affords an explanation of the remarkable properties of self-hardening and high speed steels which are chiefly tungsten steels.

On heating cementitic tungsten steels to a high temperature the particles of free carbides are dissolved the more completely the higher the temperature. Air cooling is often sufficient to retain the carbides in solution while the metal becomes finely martensitic. Such steels are said to be "self-hardening."[1] The structure of two

Fig. 18. — Tungsten steel. Tungsten 27.75 per cent. Carbon 0.276 per cent. Magnified 200 diameters. (Guillet.)

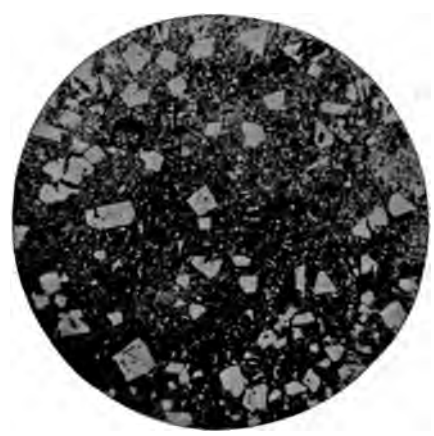


Fig. 19. — Tungsten steel. Tungsten 39.96 per cent. Carbon 0.867 per cent. Magnified 200 diameters. (Guillet.)

cementitic tungsten steels is reproduced in Figures 18 and 19. The white particles are the double carbide.

Tungsten steels are used (1) for springs generally after hardening followed by tempering, (2) for magnets after hardening only, and (3) for tools as self-hardening steels. In the latter case, however, considerable manganese is always present, the resulting alloy being in reality a quaternary steel. High speed steels are quaternary steels generally containing a large proportion of tungsten; they will soon be described.

Chrome Steels. — Chromium forms a double carbide with iron and carbon, while it has little if any direct influence on the position of the critical points.[2] The presence

[1] The presence of manganese or of a little chromium is necessary, however, to impart self-hardening properties to tungsten steel. The original "self" or "air hardening" steel, that is "Mushet" steel, always contained considerably more than one per cent manganese and was high in carbon.

[2] According to some recent observations of Nesselstrauss, chromium lowers the point Ar_3 of hypoeutectoid steels, eventually causing its disappearance while it raises a little the point Ar_1. The proportion of chromium needed to cause the point Ar_3 to disappear is the smaller, the higher the carbon content. With 0.20 per cent carbon, 5 per cent chromium are needed. With more carbon a correspondingly smaller percentage of chromium suffices.

of chromium, however, like that of tungsten causes the point on cooling to be markedly lowered as the temperature from which the metal cools increases. Osmond, for instance, found the following relations between the maximum temperature and the position of the critical point on cooling:

Maximum Temperature	Critical Point on Cooling	Maximum Temperature	Critical Point on Cooling
835	713–716	1220	635–643
1030	682–692	1320	600–640

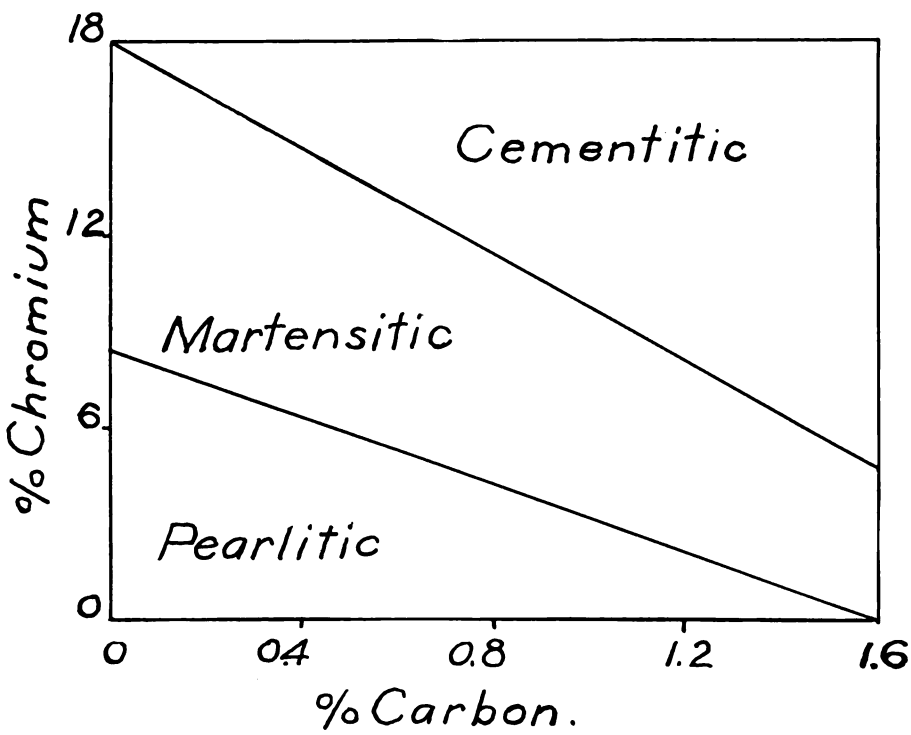


Fig. 20. — Chrome steel. Constitutional diagram. (Guillet.)

The constitutional diagram of chrome steels is shown in Figure 20 after Guillet. Reheating cementitic chrome steel to a high temperature followed by quick cooling (air or water) results generally in the disappearance of some of the particles of free carbide. The case hardening of chrome steels yields very hard cases. As the core coarsens, however, these steels should always receive the double treatment described in Lesson XVI, that is, (1) reheating and quenching for refining the core, and (2) reheating and quenching for refining and hardening the case.

The chrome steels that are utilized seldom contain more than 3 per cent chromium and are therefore pearlitic after slow cooling; they are used for the manufacture of armor piercing projectiles, of steel balls, of files, and of some other tools, the presence of chromium increasing the hardness and the hardening power of the metal.

Becker writes that the hardness imparted by chromium is not accompanied by as much brittleness as that induced by carbon. According to the same author chromium

also has the effect of increasing the elastic limit of steel, especially when it is combined with vanadium. The structure of pearlitic chromium steel resembles that of pearlitic carbon steel.

Vanadium Steels. — Vanadium forms double carbides with iron and has no marked influence on the positions of the critical points. Unlike tungsten and chromium it does not seem to cause the lowering of the Ar points with increasing temperature. The constitutional diagram of vanadium steels is shown in Figure 21 after Guillet. Two types of structures are produced, pearlitic and cementitic. Guillet describes the appearance of the particles of free carbide as being triangular.

According to Guillet heating cementitic vanadium steels to a high temperature

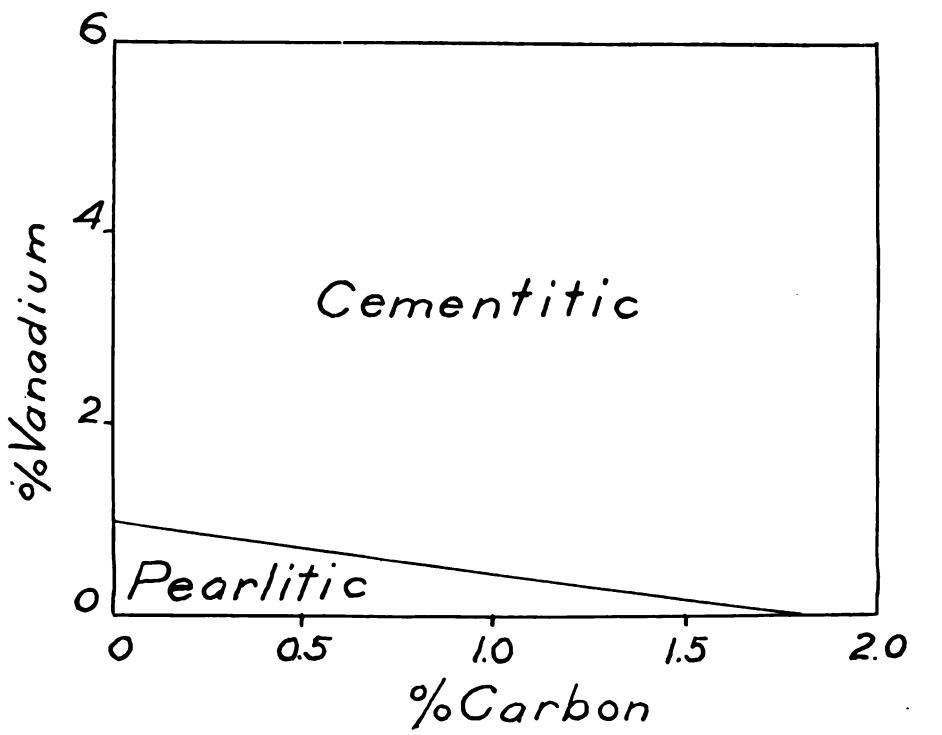


Fig. 21. — Vanadium steel. Constitutional diagram. (Guillet.)

fails to cause the absorption of the free carbide, vanadium steels differing in this respect from other steels in which double carbides are formed.

The vanadium steels commercially utilized seldom contain more than 0.50 per cent vanadium and are, therefore, pearlitic and free from carbides. Their properties recall those of pearlitic nickel steels, namely high combination of elastic limit and ductility and high resilience. The very small amount of vanadium sufficient to produce these results should be noted.

Silicon Steels. — Silicon, probably as an iron silicide, FeSi, forms a solid solution with iron in all proportions and has no very marked influence upon the position of the critical points from which we may infer that slowly cooled silicon steels will be neither martensitic nor cementitic. It is a well-known fact, moreover, that silicon has a marked tendency to cause the formation of graphitic carbon when present over a

certain proportion especially in high carbon steel. The constitutional diagram of silicon steels is shown in Figure 22 according to Guillet. It will be seen that the structure is independent of the carbon content being entirely regulated by the proportion of silicon. As long as the proportion of silicon does not exceed 5 per cent the steel is pearlitic and the whole of the carbon remains in the combined condition. Between 5 and 7 per cent of silicon some pearlite is still present and, hence, some combined carbon, but graphitic carbon also occurs; between 7 and 20 per cent of silicon the whole of the carbon is in the graphitic condition, the balance of the steel consisting of a solid solution of the silicide FeSi in iron (silico-ferrite), and also, according to

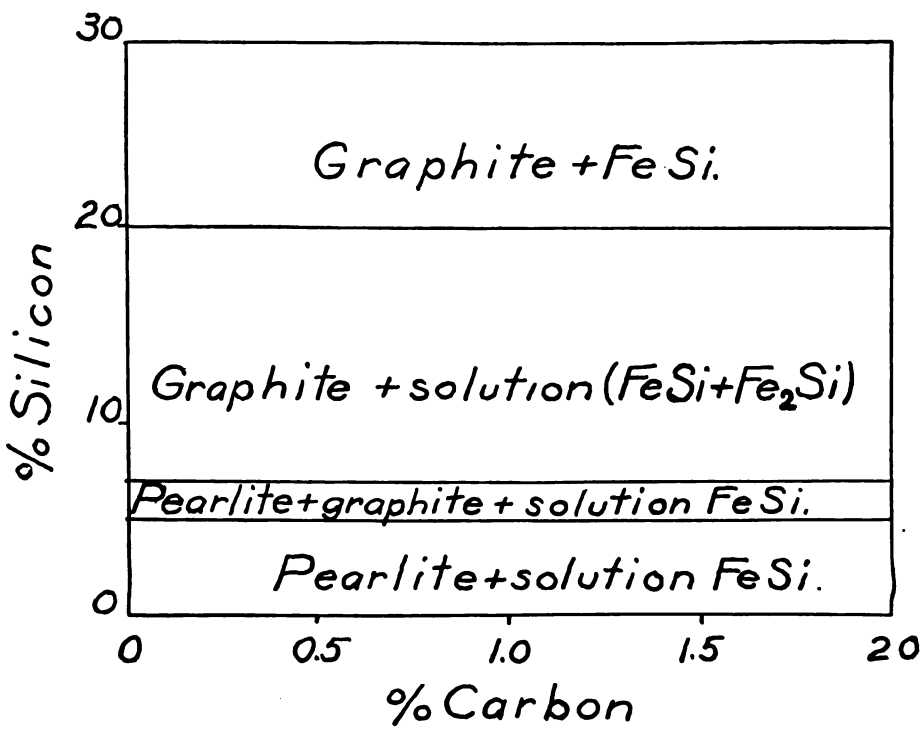


Fig. 22. — Silicon steel. Constitutional diagram. (Guillet.)

Guillet, of some Fe_2Si likewise dissolved in iron. With more than 20 per cent of silicon the steel is composed of graphite and of FeSi.

It should be noted that the only silicon steels utilized contain less than 5 per cent of silicon and are, therefore, pearlitic and free from graphitic carbon unless indeed subjected to prolonged annealing or very slow cooling when some graphitic carbon will form, especially in high carbon steels. This formation of graphitic carbon takes place the more readily the higher the temperature, the longer the time at a high temperature, the more silicon and the more carbon in the steel.

Silicon steels are chiefly used in the construction of dynamos because of their low magnetic hysteresis and high permeability and, with the addition of quite a little manganese, for springs and for certain parts of automobiles.

Chrome-Nickel Steels. — From our knowledge of the constitution of nickel steels and of chromium steels it is possible to foretell the constitution of the quaternary chrome-nickel steels. Nickel steels being pearlito-martenso-austenitic and chrome

steels being chiefly pearlito-cementitic, we may expect that in chrome-nickel steels, as the proportions of carbon, nickel, and chromium increase the steels, at first pearlitic, will become in turn martensitic, austenitic, and cementitic. In the case of cementitic steels the free carbides will be embedded in a martensitic or austenitic matrix according to their composition. It should also be expected that increasing the proportion of nickel (and carbon) will cause the steel to pass from the pearlitic to the martensitic condition, etc., while increasing the chromium (and carbon) will make it cementitic. The presence of both nickel and chromium in the same steel produces a metal possessing the valuable qualities of both nickel and chromium steels, namely, high elastic limit combined with high ductility, greater hardness, hardening power, resilience, and better wearing qualities than carbon steels. Chrome-nickel steels are especially valuable in the construction of parts to be hardened and tempered when they yield a finely martensitic structure having greater shock resisting power than the martensite of carbon steels. Practically the only chrome-nickel steels utilized are the pearlitic ones containing therefore moderate amounts of carbon, nickel, and chromium. They are used extensively in automobile construction and for the manufacture of armor plates. In the latter case, of course, one face of the plates is subjected to the case hardening treatment. The case hardening of nickel-chromium steel resembles that of nickel steel. The metal should be reheated, after the case hardening operation, slightly above the critical range of the case and quenched. Because of the presence of nickel it is not so imperative to heat to and quench from a temperature superior to the critical range of the core before hardening the case, although such procedure would probably yield a tougher core.

Quaternary Vanadium Steels. — The introduction of a small amount of vanadium into the various special steels has been strongly urged and nickel-vanadium, chrome-vanadium, chrome-nickel-vanadium and chrome-tungsten-vanadium steels have been used. It is claimed that the presence of a small proportion of vanadium (less than 0.50 per cent) increases the soundness of castings and their freedom from occluded gases and that it adds to the desirable physical qualities of forgings such as strength, resilience, ductility, etc. Guillet writes that nickel-vanadium steel properly hardened by quenching is relatively so tough that, unlike other hardened steels, it does not require tempering. Since vanadium forms a double carbide with iron its presence in steel is likely to make it cementitic. In nickel steel and in nickel-chromium steel the matrix will be pearlitic, martensitic, or austenitic in accordance with the proportion of nickel and carbon present; in chrome steels it will be pearlitic or martensitic.

Chrome-Tungsten or High Speed Steels. — Since both chromium and tungsten form carbides and since they do not lower the Ar_1 points, at least directly, it may be fairly anticipated that slowly cooled chromium-tungsten steels will be cementitic with a pearlitic, sorbitic, or even troostitic matrix. Upon being heated to a high temperature the carbide particles are dissolved and if the cooling that follows be sufficiently rapid they are retained in solution, the metal acquiring a finely martensitic structure. To cause a complete absorption of the free carbide, however, a very high temperature is often required, in some cases approaching the melting point of the steel, while air cooling is frequently sufficiently rapid to prevent the carbide from again forming. After such treatment these steels although fully hardened are in a condition relatively so stable that they may be heated to a visibly red heat, i.e. to some 600 deg. C., before their martensite undergoes any marked transformation. This invaluable property makes it possible, with tools made of such steels suitably treated, to cut

steel and other hard metals at such speed that the cutting edge of the tool becomes visibly red hot before breaking down. These steels are known in consequence as high speed steels. Their discovery by Taylor and White, at the time in the employ of the Bethlehem Steel Company, South Bethlehem, Pennsylvania, marks one of the most distinct and revolutionary advances ever made in the metallurgy of iron and steel. The composition of these steels varies greatly: they may contain from 0.25 to one per cent carbon, generally not over 0.60 per cent; from 5 to 25 per cent of tungsten, generally between 10 and 20 per cent; from 2 to 10 per cent of chromium, generally between 2 and 8 per cent, and seldom over 0.40 per cent of manganese. In some types tungsten is replaced in part or wholly by molybdenum; in others a small amount of molybdenum is present in addition to the tungsten and chromium, while in others still a small amount of vanadium (0.2 to 0.4 per cent) occurs. Properly treated high speed

Fig. 23. — High speed steel. Typical structure after correct heat treatment. Magnified 1000 diameters. (Edwards.)

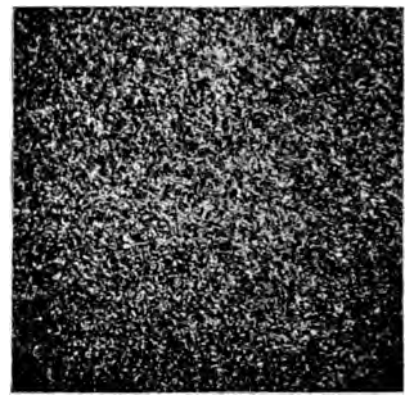


Fig. 24. — High speed steel. Typical structure after annealing. Magnified 150 diameters. (Edwards.)

steels often exhibit a polyhedric structure (Fig. 23) quite, if not altogether, free from carbide particles. The structure of a similar steel annealed is reproduced in Figure 24.

The inventors of high speed steels recommended the following treatments as yielding the best results: (1) heating the tool slowly to about 815 deg. C., then quickly until its extreme edge showed indications of melting, (2) cooling the tool quickly to below 860 deg. and then quickly or slowly to atmospheric temperature, and (3) reheating the tool to about 640 deg. for five minutes (in a lead bath) followed by cooling in air. The author believes, however, that tools of high speed steel are now generally heated to near their melting-point followed by cooling freely in air or in an air blast, a second treatment being rarely applied.

The remarkable properties of high speed steels briefly outlined in the foregoing pages must be ascribed to the formation in those steels of a martensitic structure more stable than that of quenched high carbon steel and possibly also possessing superior cutting qualities. An explanation of the greater stability and better quality of the martensite of high speed steels is suggested at least by the well-known indirect influence of chromium and tungsten on the critical points. It has been explained that while these elements have no marked direct influence upon the location of the critical points their presence causes the critical point on cooling to be lowered as the tempera-

ture from which cooling begins, increases.[1] This influence is shown graphically in Figure 25 in which the line AB represents the maximum temperatures reached before cooling and CD the position of the critical point corresponding to these temperatures. As AB ascends CD descends. If it be considered that martensite forms while the steel cools through its critical point it follows that as the steel is heated to higher temperatures its martensitic structure forms at gradually decreasing temperatures. And may we not conceive that the lower the temperature at which martensite forms the greater its stability and the better its cutting properties? Might not its superior cutting qual-

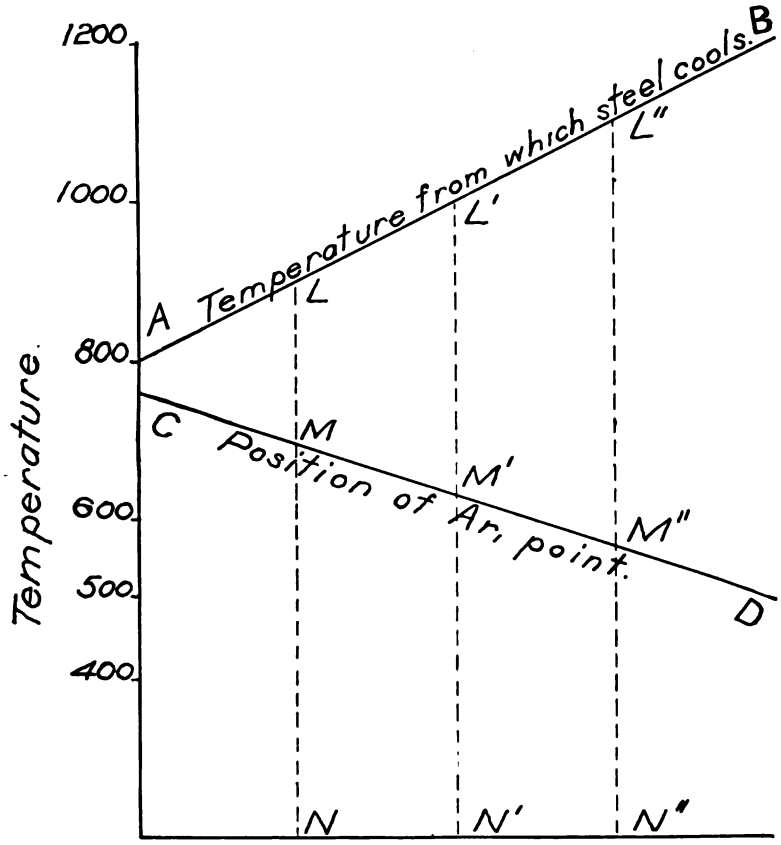


Fig. 25. — High speed steel. Relation between heating temperature, position of the Ar_1 point, and the stability of resulting martensite.

ity be due to its having been formed while the metal was cooler, i.e. stiffer and therefore opposing more effectively its transformation? It should be more stable on the ground that the greater the range of temperature between the temperature of a constituent and the point at which its transformation was due the less stable its condition. In Figure 25, for instance, the decreasing distances MN, $M'N'$, and $M''N''$ may be considered as proportional to the instability at atmospheric temperature of the martensitic structures resulting from cooling respectively from L, L', and L'' and formed in passing respectively through M, M', and M''. If this reasoning be correct it follows that the lower the temperature at which martensite is formed the greater

[1] This was shown by Osmond several years before the introduction of high speed steel and it is natural to infer that Taylor and White were guided by Osmond's discovery.

must be its stability and, therefore, the higher the temperature to which it may be heated before undergoing the tempering transformation which deprives it of its cutting properties.

Edwards believes (1) that heating high speed steel to 1200 deg. C. results in the formation of a carbide of tungsten which is dissolved by the iron, (2) that the critical point then exhibited by the steel at about 380 deg. is not the point Ar_1 lowered by the presence of tungsten and chromium but that it marks a change occurring in the carbide of tungsten, (3) that heating high speed steel to 1320 deg. C. causes the formation of a double carbide of tungsten and chromium held in solution by the iron, even in slow cooling, thus explaining the absence of critical point below 900 deg. in steel so treated, and (4) that the failing of a high speed tool is to be attributed to the formation of a new brittle constituent which can be produced by reheating the steel to 700 deg.

Experiments

The student should procure some samples of special steels, preferably the following: nickel steel containing between 3 and 3.50 per cent nickel and between 0.25 and 0.50 per cent carbon; cast manganese steel containing between 10 and 15 per cent manganese and between one and 1.5 per cent of carbon; chrome-tungsten (high speed) steel of good commercial quality.

Nickel Steel. — In its cast or forged condition the nickel steel selected is pearlitic. Its structure should be normalized by heating to 900 or 1000 deg. C. followed by slow cooling and examined. The differences in appearance between the pearlite particles and those of ordinary carbon steel subjected to like treatment (Lesson V) should be noted. Samples of this steel may be hardened and case hardened to verify the accuracy of the statements made (1) as to the lower temperature needed for hardening, and (2) as to the possibility of producing martensitic cases without quenching.

Those students who have the necessary apparatus are advised to determine the critical points of this steel comparing their results with the temperatures indicated in the lesson.

Manganese Steel. — The sample of manganese steel is austenitic. Its structure in the cast condition should be examined and should be found to contain many carbide particles, possibly forming continuous membranes around the austenite grains. A sample of this steel should be heated to 1000 or 1100 deg. and quenched in water. Its structure should now be purely austenitic (polyhedric) quite if not altogether free from carbide particles. The absence of any critical point in this steel should be ascertained; cooling from a high to atmospheric temperature should yield a smooth curve free from heat evolutions.

High Speed Steel. — The structure of this steel should be examined both in the forged condition and after reheating to some 1200 deg. followed by air cooling. The influence of tungsten and chromium in causing the lowering of the critical points as the temperature of cooling increases may be verified by those having the necessary facilities.

Photomicrographs should be taken from all structures at suitable magnifications.

Examination

Describe briefly the constitution, properties, treatments, and uses of (1) nickel steel, (2) manganese steel, (3) nickel-chromium steel, and (4) high speed steel.

LESSON XIX

CAST IRON

Cast iron differs from steel in being deprived of malleability. This lack of malleability is due to the presence of a large quantity of carbon, generally between 2.50 and 4.00 per cent. The carbon present in cast iron may be (1) wholly in the graphitic condition, (2) wholly in the combined condition, and (3) partly in the graphitic and partly in the combined condition. These three types of cast iron should be separately considered. The factors influencing the formation of graphite or of combined carbon should, however, first be recalled.

Formation of Combined and Graphitic Carbon. — It will be explained in Lesson XXIII that when cast iron solidifies the carbon probably remains in the combined condition and that the resulting carbide, Fe_3C, is partly free and partly in solid solution in the iron. This Fe_3C, however, is an unstable compound and when formed at a high temperature it is readily decomposed into graphite and iron according to the reaction

$$Fe_3C = 3\ Fe + C$$

hence the formation of graphitic carbon in cast iron. Two factors are conspicuous in promoting the formation of graphitic carbon, (1) a slow rate of cooling through and below the solidification period and (2) the presence of silicon. The gray, i.e. graphitic, cast irons are generally those which have been cast in sand and hence slowly cooled and which contain a relatively large percentage of silicon. It follows that under otherwise identical conditions and compositions a large casting will become more graphitic on solidifying than a smaller one since it will cool more slowly; also that of two castings of equal size, cooled under like conditions and of identical composition except as to their silicon contents, the one richer in silicon will contain more graphitic carbon. The conditions most effective in preventing the formation of graphitic carbon and in promoting, therefore, the retention of carbon in its combined form are (1) quick rate of cooling through and below the solidification range and (2) the presence of much sulphur or manganese.

Cast Iron Containing only Graphitic Carbon. — Cast irons containing a considerable amount of graphitic carbon are known as gray cast irons because of the appearance of their fracture which is grayish or blackish and coarsely crystalline. Cast irons containing the whole of their carbon in the graphitic condition and therefore free from combined carbon are extreme types seldom produced. Their structure, however, should be considered.

Proceeding as we did in the case of steel we shall first assume cast iron to be a pure alloy of iron and carbon, free, therefore, from its usual impurities. If the whole of the carbon is in the graphitic condition it is evident that cast iron can only contain the two constituents graphite and iron or ferrite. We may therefore anticipate its structure. It will, however, be interesting to study the mode of occurrence of the

graphitic carbon. The structure of cast iron practically free from combined carbon is illustrated both before and after etching in Figures 1 and 2. The metal will be seen to consist of an iron or ferrite matrix in which are embedded many irregular and generally elongated and curved plates of graphite. These graphite plates break up so effectively the continuity of the metallic mass as to completely destroy the ductility and malleability of a substance (ferrite) by nature very ductile and malleable. The brittleness of highly graphitic cast iron is not due so much to the brittleness of the graphite it contains nor even to its large proportion of graphite as to the thorough manner in which the continuity of its otherwise ductile matrix is destroyed by the shape and distribution of the graphite particles.

Fig. 1. — Gray cast iron free from combined carbon. Magnified 100 diameters. Not etched. (F. C. Langenberg in the author's laboratory.)

It will be seen in another lesson that when the graphite occurs in small rounded particles as it does in malleable cast iron the ferrite matrix may retain considerable ductility and malleability.

The ferrite matrix of this highly graphitic cast iron (Fig. 2) will be seen to be made up of the polyhedric crystalline grains characteristic of carbonless iron, the ferrite of cast iron being similar in this and other respects to the ferrite of wrought iron and of hypo-eutectoid steel. In impure cast iron it undoubtedly holds in solution silicon and possibly, to some extent, other impurities.

Highly graphitic cast iron is brittle and deprived of ductility and malleability because of the presence of numerous plates of graphitic carbon; it is weak because of the presence of graphite plates and because of the relative weakness of its matrix; it is soft and therefore easily machined because of the softness both of its matrix and of the graphite it contains; it expands on solidifying because of the formation, with

increase of bulk, during solidification of a large amount of graphitic carbon. It should be noted that because of its low specific gravity graphite will occupy a relatively large proportion of the bulk of the metal. Cast iron, for instance, containing by weight 3 per cent of graphite contains by volume some 12 per cent of that element.

As might be expected the rate of solidification and further cooling has some influence both upon the shape and size of the graphite particles as well as upon the size of the ferrite grains, and therefore upon the physical properties of the metal, very slow solidification promoting the formation of large graphite plates and of large ferrite grains. Were it possible to cause the graphite in cast iron to occur in small rounded

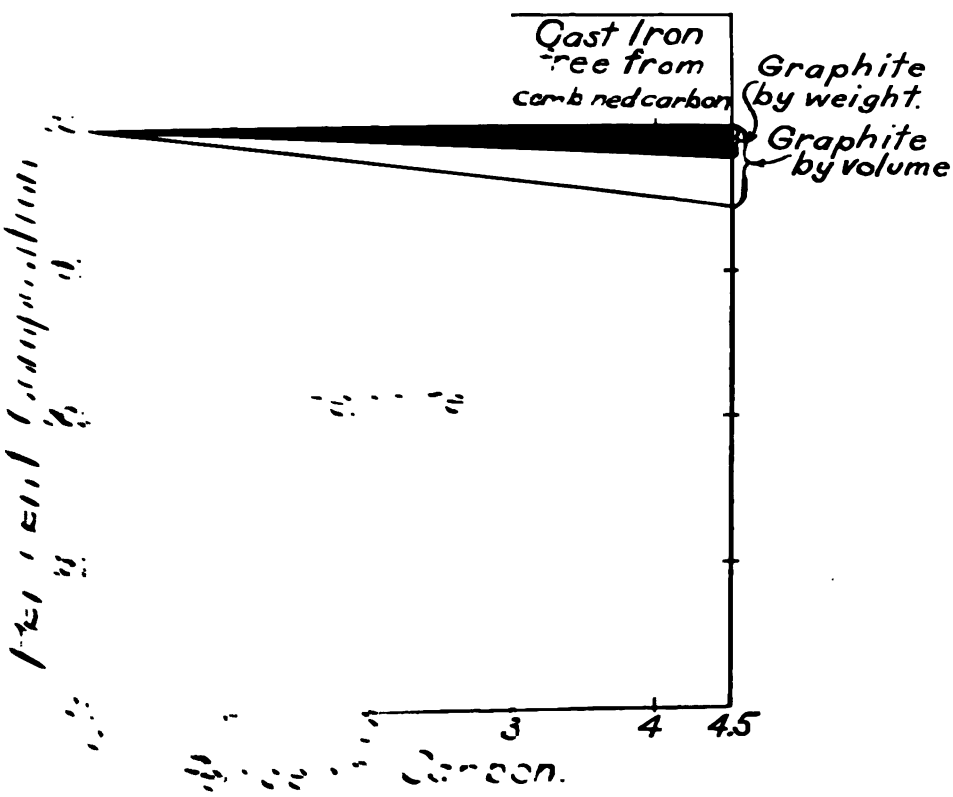
Fig. 2. — Same metal as in Fig. 2. Magnified 100 diameters Etched. (F. C. Langenberg in the author's laboratory.)

particles instead of as sharp, curved plates, its ductility and strength would undoubtedly be greatly increased.

The diagram of Figure 3 shows graphically the structural composition of iron-carbon alloys in which the whole of the carbon occurs as graphite. Only those alloys, however, containing from 3 to 4.5 per cent carbon can be produced. Indeed in the absence of silicon even these are quite unobtainable. With less than 3 per cent carbon it is well nigh impossible to prevent the retention of some combined carbon, while with less than 2 or at least with less than 1.50 per cent carbon the whole of the carbon is likely to be in the combined condition. The diagram, therefore, is only a theoretical one. It has, nevertheless, its interest for it will be shown in another lesson to represent the stable and final equilibrium of the iron-carbon system. The percentage of graphite by volume has also been indicated.

Cast Iron Containing only Combined Carbon. — Cast iron containing only combined carbon and free, therefore, from graphitic carbon is called "white" cast iron

... white, brilliant, and highly metallic. The ... the presence of much manganese ... quick cooling through and below the solidifica- ... high manganese and sulphur, and quick solidi- ... much sulphur and manganese and ... solidification or it may solidify so quickly ... silicon and little manganese and sulphur. ... the rate of cooling is afforded by the ... cast iron which if cast in sand would



... alloys free from combined carbon.

... castings since they cool more quickly

... ure of cast iron should resemble the ... consist after slow cooling of pearlite ... is found to be the case as shown in ... white iron containing about 3 per cent ... should contain nearly 63 per cent of ... dark constituent in the photograph ... cementite. The structure of white cast ... magnification, the laminations of pearlite ... cast iron is further illustrated in Figures ... graphs are reproduced here because they

afford an interesting example of the action of sodium picrate (Lesson V, page 7) in coloring free cementite while leaving pearlite uncolored.

The structural composition of white cast iron is to be calculated like the composition of any hyper-eutectoid steel of known carbon content as explained in Lesson V, the following relation existing between the percentage of pearlite and that of carbon in the iron, on the assumption that pearlite contains 0.834 per cent carbon:

$$P = \frac{800 - 120\ C}{7}$$

the balance of the metal being of course free cementite. While structurally it resembles high carbon steel, white cast iron is deprived of malleability being indeed very brittle and very hard. This brittleness and hardness are due to the very large proportion of free cementite present which itself is very hard and brittle.

Fig. 4. — White cast iron. Magnified 56 diameters.

Fig. 5. — White cast iron. Magnified 500 diameters. (Wüst.)

It will be evident that, starting from carbonless iron, as the carbon increases at first low carbon steel is produced and then in succession medium high carbon steel, high carbon steel, and finally white cast iron, each metal passing gradually into the next without any sharp line of demarcation between them. It is logical to base the distinction between high carbon steel and white cast iron upon the malleability of the former and the non-malleability of the latter and this is altogether a question of carbon content. The dividing line may be drawn somewhat arbitrarily at 2 per cent carbon. As a matter of fact steels are very seldom manufactured containing more than 1.75 per cent carbon while white cast iron rarely contains less than 2.25 per cent carbon. Between the steel series, therefore, and the white cast-iron series there is a natural gap, the existence of which generally removes any doubt as to the nature of the metal under examination.

Again if the process of manufacture be known there need be no doubt as to the classification of any highly carburized iron alloy: if made in the blast furnace from

... are indicated in the ...
... pro-eutectoid or free ferrite, the ...
... of cementite are to be ...
... 2 pro-eutectoid cementite, 3 ...
... the sum of all four being known as to

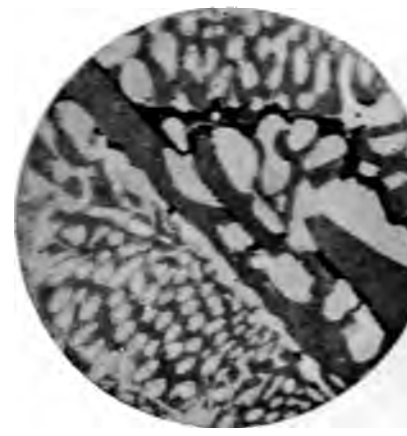


Fig. 7. —Same metal as in Fig. 6. Mag
fied 200 diameters. Etched with sodi
picrate. (Guillet.)

... as free cementite. Let us recall the meanir

... ferrite included in pearlite.
... ferrite liberated as hypo-eutectoid steel coo
... or $Ar_{3.2}$) to its lower point (Ar_1).
... the cementite included in pearlite.
... cementite that is liberated as hyper-eutectoid met
... point Ar_{cm}) to its lower point ($Ar_{3.2.1}$).
... included in the austenite-cementite eutecti
... sation of alloys containing more than some 1.7
... XXIII.
... cementite which forms between the beginning an
... alloys containing more than 4.3 per cent carbon :
... calls it "primary" cementite.
... corresponding respectively to the steel series and t
... been indicated leaving two groups of alloys un

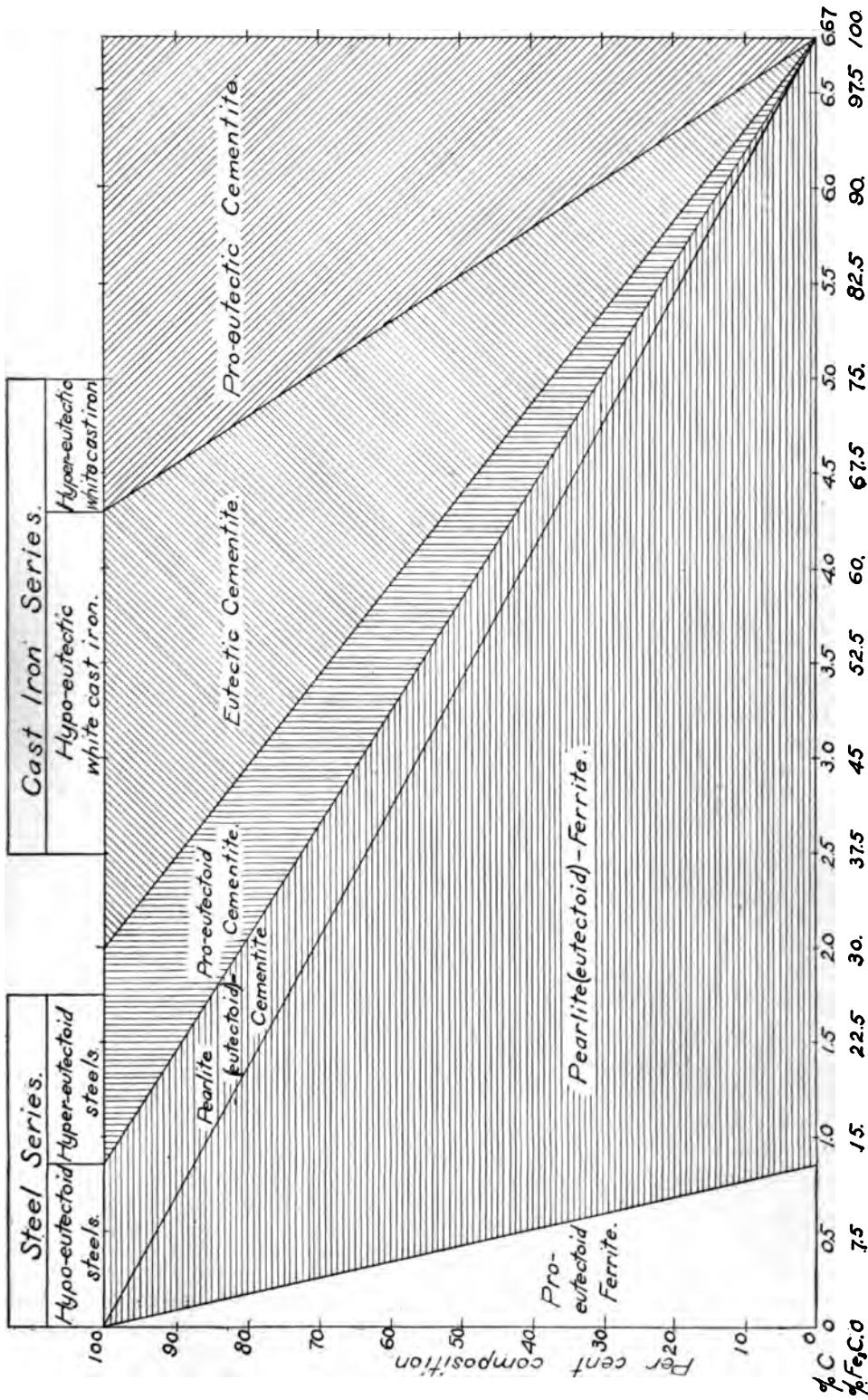


Fig. 8. — Structural composition diagram of iron-carbon alloys free from graphitic carbon.

[illegible] by [illegible] namely, those containing between 1.70 per cent and [illegible] per cent carbon and those containing more than 5 per cent of carbon.[1] The [illegible] of this diagram has been used in Lesson V.

Cast Iron Containing both Combined and Graphitic Carbon. — Cast-iron castings [illegible] both combined and graphitic carbon. In the majority of cases [illegible] per cent of combined carbon, the balance of that element [illegible] graphitic condition. The chief factors affecting this distribution [illegible] between the combined and the graphitic states have already been alluded [illegible] the rate of cooling during and below solidification (hence the size of the castings and [illegible] the presence of silicon, manganese, and sulphur, the first element promoting and the last two opposing the formation of graphitic carbon. If it be

Fig. [illegible] Gray cast iron. Hypo-eutectoid matrix [illegible] per cent combined carbon. Magnified 100 diameters. Boylston.

[illegible] that graphitic carbon is soft, 2 that the presence of much graphite, [illegible] means the occurrence of soft ferrite in the cast [illegible] combined carbon (cementite) is very hard, and (4) as later explained, [illegible] presence of combined carbon, at least up to a certain proportion, greatly increases the strength of cast iron, it will be evident that the physical properties of cast [illegible] strength and hardness, will depend chiefly upon the proportion of [illegible] and graphitic carbon it contains.

[illegible] consider the structure of cast iron containing a small amount, say 0.25

[illegible] that we are considering here pure alloys of iron and carbon. In the [illegible] or chromium iron may contain as much as 6.50 per cent and even much [illegible] the absence cast iron very seldom contains more than 4.5 per cent carbon. [illegible] are offered for sale under the name of semi-steel which may contain [illegible] of total carbon entirely combined, forming, therefore, a sort of connect- [illegible] and the cast-iron series. They are frequently obtained by remelting cast [illegible] the presence of considerable iron or steel scrap. Washed metal likewise [illegible] per cent of total and entirely combined carbon but this is a [illegible] a partial refining only of cast iron.

per cent, of combined carbon and some 3 per cent of graphitic carbon (Fig. 9). The combined carbon will yield 15 times its own weight of cementite ($0.25 \times 15 = 3.75$ per cent) and the resulting cementite eight times its own weight of pearlite ($3.75 \times 8 = 30$ per cent), or more quickly,

$$0.25 \times 120 = 30 \text{ per cent pearlite}$$

exactly as in the case of steel.

The cast iron under consideration will therefore contain 30 per cent pearlite, 3 per cent of graphite, and the balance, 67 per cent, necessarily free ferrite. Cast iron containing graphitic carbon may be considered as being made up of two distinct parts, namely, (1) graphite and (2) a metallic matrix in which the graphite particles are embedded. It will be obvious, moreover, that the metallic matrix of gray cast iron is in reality a steel matrix since it necessarily consists, like steel, of an aggregate of

Fig. 10. — Gray cast iron. Eutectoid matrix. Magnified 500 diameters. (Boylston.)

ferrite and cementite partly associated to form pearlite. In cast iron free from combined carbon the matrix is pure ferrite; with a little combined carbon it is of the nature of a low carbon steel; as the combined carbon increases the metallic matrix is converted into steel of increasing carbon content; with less than some 0.80 per cent carbon the matrix resembles an hypo-eutectoid steel; with some 0.80 per cent carbon the matrix is pure pearlite, i.e. eutectoid steel; with more than 0.80 per cent carbon some free cementite is formed, the matrix consisting of hyper-eutectoid steel. In other words, as the proportion of combined carbon increases, structural changes take place in the metallic matrix of cast iron identical to those observed and described in the case of steel. The structure of cast iron containing increasing proportion of combined carbon is illustrated in Figures 9 to 11.

The above considerations justify us in considering gray cast iron as steel, that is, as an aggregate of ferrite and cementite, the continuity of which is destroyed by the presence of numerous graphite plates, the enormous difference in properties between

cast iron and steel being due solely to the presence of this graphitic carbon or rather to the breaking of the continuity of the mass which it implies. To illustrate further, if it were possible to remove bodily from a chunk of cast iron every particle of graphite, its strength and ductility would not probably be greatly increased because its continuity would still be effectively destroyed by the empty spaces once occupied by graphite. If not too high in carbon, however, it would now be weldable and could be forged into a small piece of steel, or it could be remelted and cast into a sound steel casting.

Mottled Cast Iron. — Cast irons are sometimes produced that are partly gray and partly white, that is made up of particles containing graphitic carbon and of particles free from graphite — their structure is well shown in Figure 12. They are called "mottled" because of the appearance of their fracture.

Fig. 11. — Gray cast iron. Hyper-eutectoid matrix. Magnified 500 diameters. (Wüst.)

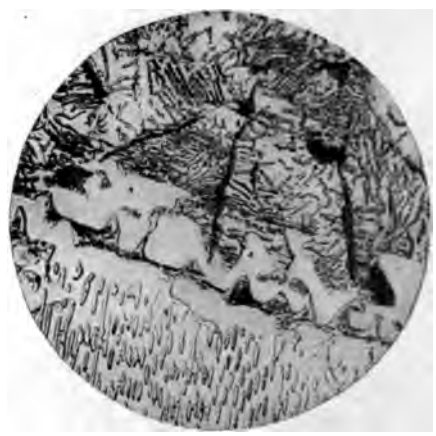


Fig. 12. — Mottled cast iron. Magnified 500 diameters. (Wüst.)

Structural Composition of Cast Iron. — The structural composition of any cast iron of known percentages of graphitic and combined carbon can readily be calculated by following the method employed in the case of steel and assuming pearlite to contain 0.834 per cent carbon, that is, exactly one part by weight of cementite and seven parts of ferrite. It should be noted, however, that in the presence of graphite it requires a smaller proportion of carbon to convert the whole matrix into pearlite since there is less iron to be so converted. To make the matter clear in order that cast iron may be free from both excess ferrite and excess cementite it must contain ferrite and cementite in the exact proportion of one part of cementite to seven of ferrite. If the cast iron contains G per cent of graphite and C per cent of combined carbon forming 15C per cent of cementite the balance of the metal, 100 – G – 15C, will be ferrite. Consequently if

$$100 - G - 15C = 7 \times 15C = 105C$$
$$\text{or } 100 - G - 120C = 0$$

that is, if the proportion of ferrite equals seven times that of cementite the matrix will contain pearlite only; if 100 – G – 120C is greater than 0 the matrix will be hypo-eutectoid; if 100 – G – 120C is smaller than 0 the matrix will be hyper-eutectoid.

In the presence of 3 per cent graphite, for instance, the following relation will indicate the needed percentage of combined carbon to make the matrix entirely pearlitic:

$$100 - 3 - 120C = 0$$

which gives for C very nearly 0.80 per cent.

It will be sufficiently accurate to assume in every case that gray cast iron containing less than 0.80 per cent combined carbon has an hypo-eutectoid matrix while cast iron containing more combined carbon has an hyper-eutectoid matrix.

In calculating the structural composition of cast iron two cases then should be considered, (1) the cast iron contains less than 0.80 per cent combined carbon; it has an hypo-eutectoid matrix and (2) it contains more than 0.80 per cent combined carbon; it has an hyper-eutectoid matrix. In the first instance we have the following relations between the percentage of graphitic carbon, G, the percentage of combined carbon, C, the percentage of ferrite, F, and the percentage of pearlite, P,

$$(1)\ F + P + G = 100$$
$$(2)\ P = 8 \times 15C = 120C$$

If C = 0.50 per cent, for instance, and G = 3 per cent, the iron would contain 60 per cent pearlite, 37 per cent ferrite, and 3 per cent graphite.

If the iron has an hyper-eutectoid matrix, that is if it contains more than 0.80 per cent of combined carbon, we can write the following equations, Cm representing the percentage of free cementite,

$$(1)\ P + Cm + G = 100$$
$$(2)\ P = \tfrac{8}{7}F = \tfrac{8}{7}(100 - G - 15C)$$

the second equation expressing the fact that the totality of the ferrite (100 – G – 15C) is included in the pearlite and that the percentage of pearlite is equal to $\frac{8}{7}$ times that of ferrite. If cast iron contains 2 per cent of graphite and 1.25 per cent of combined carbon, for instance, the foregoing equations indicate the following structural composition: pearlite 90.60 per cent, free cementite 7.40 per cent, and graphite 2 per cent.

The structural, graphical diagram of cast iron containing both combined and graphitic carbon has been constructed in Figure 13 in accordance with the scheme followed in these lessons. It is assumed in this diagram that the total carbon remains constant at 3.50 per cent and that the amount of combined carbon increases from 0 to 3.50 per cent, in this way including the two extreme cases corresponding respectively to absence of combined carbon and of graphitic carbon. If this diagram be compared with that of the structural composition of steel, Lesson V, p. 13, the steel nature of the metallic matrix of cast iron will be apparent. It will be noted that in the present diagram when the proportion of combined carbon exceeds 1.7 per cent there are two sources of free cementite indicated, namely, pro-eutectoid cementite and eutectic cementite; the origin of the latter will be made clear in Lesson XXIII. Both of these cementites constitute the free cementite present in cast iron, containing more than 1.7 per cent of combined carbon; while formed, as later explained, at different periods of the cooling, they appear to coagulate together and cannot be distinguished from each other under the microscope.

Physical Properties of Cast Iron vs. its Structural Composition. — The physical properties of cast iron must necessarily depend to a very great extent upon the properties of its steel matrix from which it follows that its hardness and strength will increase with increasing combined carbon, the hardness indefinitely, the strength up

to the eutectoid carbon ratio. It is evident, therefore, that cast iron of maximum strength (1) should have a steel matrix of maximum strength, i.e. should contain in the vicinity of 0.80 per cent combined carbon and (2) should contain as little graphitic carbon as possible since every graphite particle is a source of weakness; in other words, the nearer cast iron approaches a steel of maximum strength the greater will be its strength. After having secured the desired amount of combined carbon to give strength it is evident that a reduction of the graphitic carbon must mean a corresponding reduction of the total carbon in cast iron. In ordinary cupola practise for the production of cast-iron castings, however, which consists in remelting pig iron of

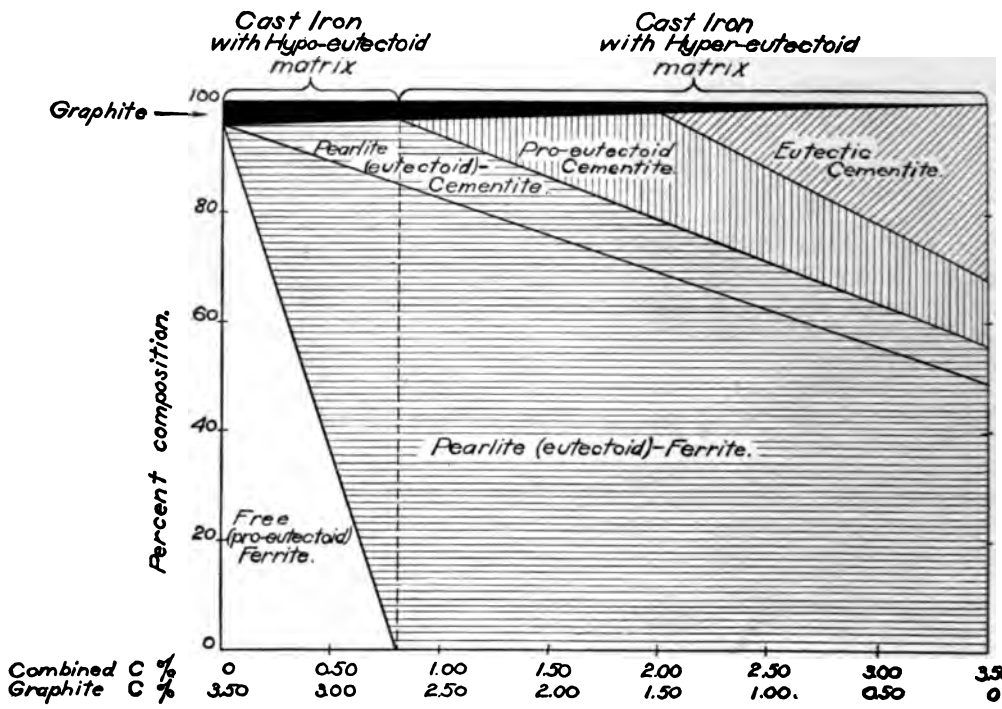


Fig. 13. — Structural composition diagram of iron-carbon alloys containing a constant proportion of total carbon (3.50 per cent), but varying percentages of combined carbon (from 0 to 3.50 per cent.)

suitable composition, the proportion of total carbon is difficult to control, being necessarily between 3 and 4 per cent and we must depend to produce strength almost altogether upon the retention in the combined condition of a suitable proportion of carbon. The total carbon may be decreased, however, by the use of iron and steel scrap as part of the burden of the cupola resulting in increased strength, for same percentage of combined carbon, or by remelting in a so-called "air furnace," i.e. under oxidizing conditions when part of the carbon is burnt out. These low total carbon, and therefore tenacious, cast-iron castings are sometimes offered for sale under the name of semi-steels, a practise somewhat misleading for they are not steel in any sense of the word since they are not malleable, have very little ductility, and generally contain a considerable amount of graphitic carbon.

If soft cast-iron castings are desired so that they may be easily machined they should contain as little combined carbon as possible. In the presence of but little

combined carbon, however, the iron will not be very tenacious, strength and softness being antagonistic. If the castings are to be hard they should contain much combined carbon and, therefore, little graphite. In extreme cases they will be free from graphite, when their hardness will be very great, but they will then also be very brittle. In the majority of cases castings are wanted soft enough to be easily machined and at the same time of fair strength. This combination of properties is evidently to be obtained by producing a matrix corresponding to a medium high carbon steel, i.e. by causing the cast iron to retain some 0.30 to 0.60 per cent of combined carbon.

The percentage of combined carbon in cast iron upon which its physical properties primarily depend, can be ascertained more quickly and readily by microscopical examination than by chemical analysis and quite as accurately.

Chilled Cast-Iron Castings. — It is sometimes desired to produce cast-iron castings very hard near their outside but soft and relatively tough near their center. This may be done by so regulating the composition and solidification as to prevent the formation of graphite in those portions that should be hard while allowing it to form in the portions that should be soft. The means generally employed consist in using iron plates for those parts of the molds corresponding to the parts of the castings that are to be hard and sand for the other parts, the quicker solidification and further cooling of the metal coming in contact with the iron plates causing the retention of much combined carbon. The resulting castings are known as "chilled" castings. Important instances of the application of this method are to be found in the manufacture of chilled cast-iron wheels and of chilled rolls. It will be evident that the presence of sulphur and manganese in the cast iron should promote the retention of combined carbon on quick cooling while the presence of silicon and of large percentages of total carbon should hinder it. The chemical composition of cast iron to be converted into chilled castings should therefore be carefully regulated. Microscopical examination should prove of much value in examining the depth and quality of "chills."

Examination

I. Describe the structure of cast iron containing both graphitic and combined carbon and compare it to that of steel.

II. Assuming pearlite to contain 0.83 per cent carbon what will be the structural composition of cast iron containing 3.25 per cent graphite and 0.40 per cent combined carbon and of cast iron containing 1.90 per cent graphite and 1.60 per cent combined carbon?

III. Describe with explanation what should be the structure and composition (as far as carbon is concerned) of cast iron with the following properties: (1) Very soft but weak, (2) very hard but brittle, (3) very strong but lacking in softness, and (4) combining moderate strength with moderate softness.

LESSON XX

IMPURITIES IN CAST IRON

In the preceding lesson cast iron has been considered as a pure alloy of iron and carbon, but like steel, commercial cast iron always contains varying proportions of silicon, manganese, phosphorus, and sulphur, and we should now examine the influence of these impurities on its structure and consequently on its properties.

Silicon in Cast Iron. — Cast iron seldom contains less than 0.50 per cent silicon and frequently as much as 3 or 3.50 per cent. As in the case of steel this silicon probably combines with some of the iron to form the silicide of iron, FeSi, which is then dissolved in the balance of the iron. The ferrite of cast iron, therefore, always holds a considerable amount of silicon or rather of the silicide FeSi in solution. It has been seen that silicon produces exactly three times its own weight of FeSi; cast iron with 2 per cent of silicon, for instance, will contain 6 per cent of FeSi dissolved in its ferrite. The influence of silicon on the properties of cast iron is very important chiefly through its promoting the formation of graphitic carbon and, therefore, increasing the softness and, if carried too far, decreasing the strength of cast iron. It is why foundrymen often speak of silicon as a "softener." That it increases fluidity while decreasing shrinkage and chill is also well known.

The occurrence of varying amounts of silicon in cast iron cannot be detected under the microscope, unless indirectly and roughly through the presence of more or less graphitic carbon. It is probably true, however, that under otherwise similar conditions, the more silicon present in ferrite the slower the etching of that constituent. The ferrite of cast iron with hypo-eutectoid matrix, for instance, possibly because of its greater silicon content, often remains brilliant after the usual deep etching treatment which would color decidedly some of the grains of the ferrite of wrought iron or of low carbon steel.

Sulphur in Cast Iron. — Cast-iron castings of good quality should not contain more than 0.1 per cent of sulphur while but a trace of that element may be present. In the manufacture of chilled castings, however, as much as 0.2 per cent sulphur is sometimes allowed. It has been explained in Lesson VI that because of the great affinity of manganese for sulphur these two elements readily combine to form the manganese sulphide MnS, each part by weight of sulphur giving rise to the formation approximately of 2½ parts of MnS. Cast iron with 0.05 per cent sulphur, for instance, would contain about 0.125 per cent of MnS. As in the case of steel this sulphide occurs in the form of rounded particles of a dove gray or slate color embedded in the metallic matrix (Fig. 1). Should there not be enough manganese present to combine with all the sulphur, the remaining sulphur would unite with iron to form the sulphide FeS which would occur as rounded yellow areas. It should be noted, however, that since it requires less than two parts by weight of manganese to combine with one part of sulphur, when cast iron contains twice as much manganese as it does sulphur no iron sulphide can be formed, theoretically at least. Since it is seldom that

cast iron does not contain a considerably greater proportion of manganese the occurrence of FeS in cast iron should be rare.

The influence of sulphur in opposing the formation of graphitic carbon has already been mentioned; it may consequently be said to harden cast iron. It has also a well-known influence in increasing the depth of "chill" in solidifying cast iron against a metal wall, that is the thickness of metal free from graphitic carbon produced by the cooling action of that wall. Its other influences are harmful as it increases shrinkage, causes the molten metal to be sluggish, and induces unsoundness.

Manganese in Cast Iron. — Special cast irons are made, known as spiegeleisen, ferro-manganese, etc., containing very large proportions of manganese, but in ordinary castings the amount of manganese seldom exceeds 2 per cent and may be as low as 0.10 per cent. It has been shown in Lesson VI that when manganese is present in

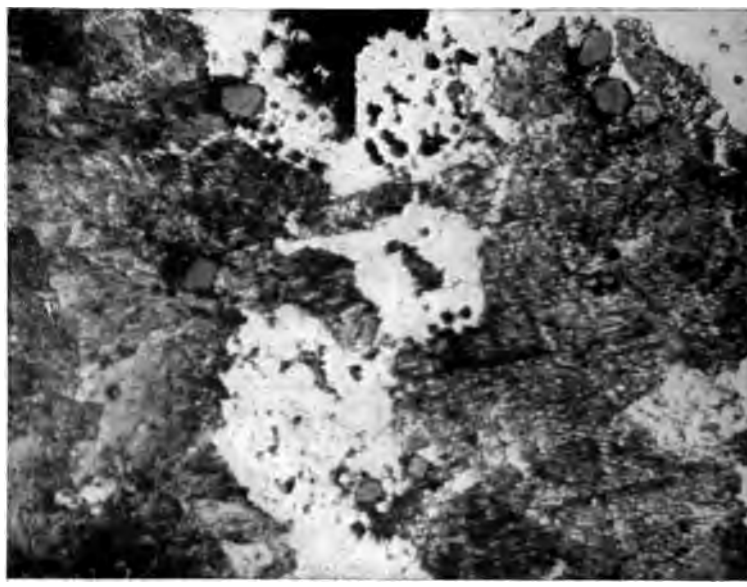


Fig. 1. — Partially malleablized cast iron. Magnified 670 diameters. Sulphur about 0.2 per cent, manganese 0.50 per cent. (C. C. Buck, Correspondence Course student.)

these relatively small proportions it first combines with sulphur to form the sulphide MnS, and then with carbon to form the carbide Mn_3C, this carbide uniting with the carbide Fe_3C to form cementite. The cementite of cast iron, therefore, like that of steel nearly always contains some Mn_3C. Since iron and manganese, however, have nearly the same atomic weights it remains true that to obtain the percentage of cementite in any commercial iron-carbon alloy it suffices to multiply its percentage of combined carbon by fifteen.

The influence of manganese in opposing the formation of graphitic carbon has already been noted; like sulphur it is a hardener, its presence in large proportions increasing the difficulty of machining castings. It promotes the absorption of carbon by iron. Some believe that it increases shrinkage and that while it has no marked influence on the depth of the chill it increases its hardness.

Phosphorus in Cast Iron. — It has been explained in Lesson VI that when phosphorus occurs in very small quantities as it does in steel, the totality of it probably

forms the phosphide Fe_3P, which is then dissolved by the iron. In cast iron, however, because of the frequent presence of a considerable proportion of phosphorus and of a larger proportion of carbon this element assumes another condition. The occurrence of phosphorus in cast iron was first studied and described by Stead. The results of his important investigations are briefly summarized below:

(1) When phosphorus is alloyed with carbonless iron in amount varying from traces to 1.70 per cent, it forms a phosphide corresponding to the formula Fe_3P, which is held in solid solution by the iron. All the metals used commercially, such as wrought iron and steels containing very little carbon, may be included in this class. They consist essentially of polyhedric grains of ferrite holding Fe_3P in solution.

(2) When the metal contains from 1.70 to 10.2 per cent phosphorus it consists of a saturated solution of Fe_3P in iron (1.70 per cent P) and of a eutectic alloy containing about 10.2 per cent P and made up of about 61 per cent Fe_3P and 39 per cent of the

Fig. 2. — Alloy of iron and phosphorus. Phosphorus 1.8 per cent. Magnified 350 diameters. (Stead.)

Fig. 3. — Alloy of iron and phosphorus. Phosphorus 8 per cent. Magnified 250 diameters. (Stead.)

saturated solution of Fe_3P in iron. To account readily for this structure and that of the following groups, it is only necessary to consider these metals as alloys of two constituents: one the phosphide Fe_3P, and the other a saturated solution of Fe_3P in iron. It is well known that a certain class of binary alloys when solidifying give rise to the formation of a eutectic alloy, that is, of a mechanical mixture made up in definite proportions, of extremely small plates alternately of one and the other constituents, the balance of the mass consisting of that constituent which is present in excess over the amount required to form the eutectic alloy. It is precisely what happens in the case of iron containing over 1.70 per cent phosphorus. The formation of eutectic alloys will be further described in Lesson XXII. For the iron-phosphide eutectic discovered by Stead the author in 1901 suggested the name of "Steadite."

Figures 2, 3, and 4 illustrate the structure of iron containing respectively 1.8, 8, and 10.2 per cent phosphorus. The mottled constituent made up of two structural elements in close juxtaposition corresponds in every case to the phosphide eutectic. The background of Figure 2 and the clear regions of Figure 3 are composed of the solid saturated solution, while Figure 4 is composed entirely of the eutectic alloy.

(3) When the iron contains from 10.2 per cent to 15.58 per cent phosphorus it is composed of crystals of Fe_3P surrounded by the eutectic mixture just described, as illustrated in Figure 5, in which the white angular areas represent Fe_3P and the background the eutectic alloy.

(4) Describing the influence of carbon on the structure of iron-phosphorus alloys, Stead wrote:

"On melting saturated solid solutions of phosphide of iron in iron with carbon, the latter causes a separation of the phosphide near to the point of solidification, which appears in the solid metal as a eutectic in irregular-shaped areas, if the carbon present is small, and in envelopes, increasing in thickness with the amount of carbon present, but is incapable of throwing the whole of the phosphide out of solution even when 3.5 per cent C is present. A residuum always remains in solid solution. This residuum is smallest, however, when the carbon is at a maximum."

Fig. 4. — Alloy of iron and phosphorus. Phosphorus 10.2 per cent. Magnified 350 diameters. (Stead.)

Fig. 5. — Alloy of iron and phosphorus. Phosphorus 11.07 per cent. Magnified 60 diameters. (Stead.)

These conclusions are illustrated in Figures 6, 7, and 8, showing the structure of some samples of iron with 1.7 per cent phosphorus, and containing respectively 0.18, 0.71, and 1.4 per cent C.

It will be obvious from the above description of the behavior of phosphorus that in cast iron, because of the presence of a large amount of carbon, nearly the whole of the phosphorus is liberated from its solution with iron and caused to occur as the phosphide eutectic or steadite, even if the metal contains less than the necessary amount of phosphorus needed to saturate the iron, namely 1.70 per cent. Indeed so marked is this action of carbon that Stead tells us that in steel containing but 0.1 per cent phosphorus a portion of it is liable to be thrown out of solution in the presence of 0.90 per cent carbon.

To sum up, the phosphorus in ordinary steels occurs chiefly and probably altogether as the phosphide Fe_3P dissolved in iron while in cast iron it occurs chiefly if not entirely as a eutectic the constituents of which are (1) a solid solution of iron and 1.70 per cent of phosphorus and (2) the phosphide Fe_3P. While Stead writes that the whole of the phosphorus is not liberated from solution even in the presence of much

carbon, the amount retained in solution in the presence of some 3 per cent or more carbon is apparently very small and it may probably be assumed for all practical purposes that in cast iron the whole of the phosphorus is present as a eutectic, for Stead says that the phosphide eutectic may be detected in cast iron containing as little as

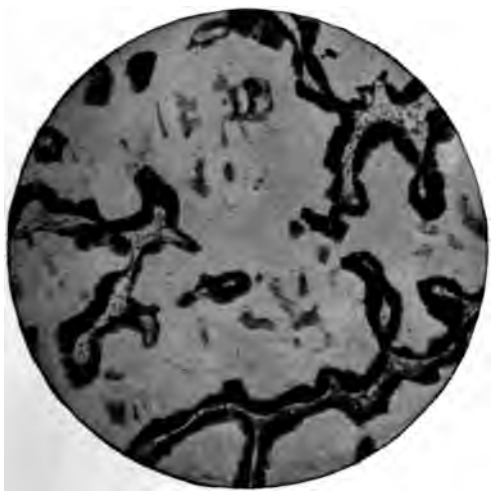


Fig. 6. — Alloy of iron, phosphorus, and carbon. Phosphorus 1.74 per cent, carbon 0.18 per cent. Magnified 60 diameters. (Stead.)

Fig. 7. — Alloy of iron, phosphorus, and carbon. Phosphorus 1.70 per cent, carbon 0.71 per cent. Magnified 250 diameters. (Stead.)

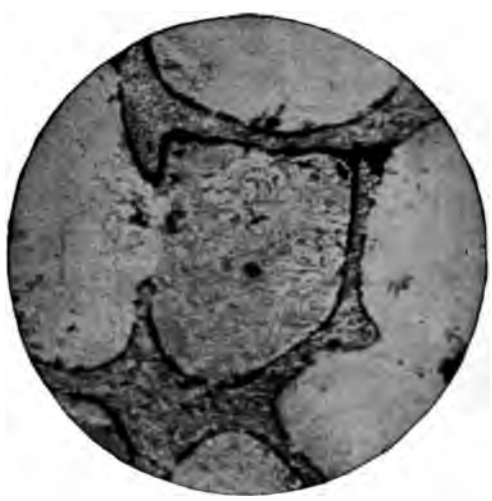


Fig. 8. — Alloy of iron, phosphorus, and carbon. Phosphorus 1.70 per cent, carbon 1.40 per cent. Magnified 250 diameters. (Stead.)

0.03 per cent phosphorus. The structure of phosphoretic cast iron is illustrated in Figures 9 and 10. The various constituents, graphite, pearlite, free ferrite, and steadite are easily distinguishable. The first sample has a hypo-eutectoid matrix, the second a eutectoid matrix.

Stead recommends heat tinting as a suitable treatment for bringing out the phosphide eutectic especially in white cast iron when there is danger of confounding

[illegible] will be found described in an [illegible]

[illegible] high proportion of phosphorus [illegible]

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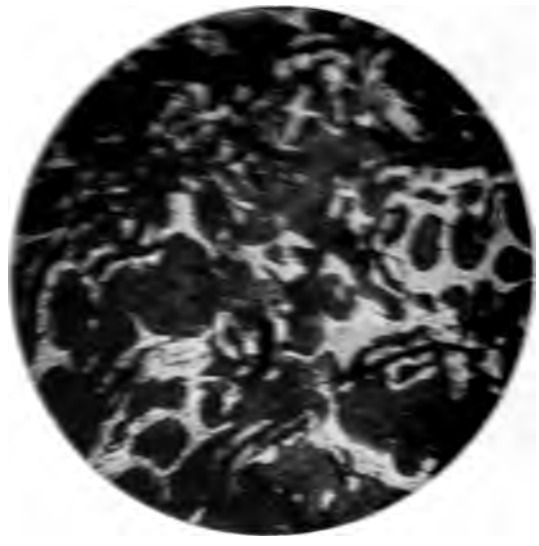

Fig. 10. [illegible] Magnified 100 diameters. Graphite, pearlite, and steadite. Boylston.

"The reason why phosphoretic pig irons are not more brittle than they are is because the eutectic separates into isolated segregations, and does not form continuous cells around the crystalline grains. When the phosphorus does not exceed 1.1 per cent the metal is comparatively strong, but an addition of 0.3 per cent reduces the strength materially, the reason of which is that the eutectic brittle areas in metal

with 2 per cent phosphorus approach each other closely, leaving less of the strong ground mass intervening."

Phosphorus has no marked influence upon the condition in which carbon occurs in cast iron but it increases the fluidity of the metal probably because of the formation of a large quantity of fusible and fluid phosphide eutectic.

Structural Composition of Phosphoretic Cast Iron. — Since the presence of 10.2 per cent phosphorus causes the production of 100 per cent steadite it follows that the phosphorus in cast iron gives rise to the formation of approximately 10 times its own weight of steadite.

In calculating the structural composition of cast iron, therefore, the amount of phosphorus present must be considered as it may very materially lower the percentage of combined carbon needed to convert its matrix into pearlite. Bearing in mind that cast iron to be free from both free ferrite and free cementite must contain ferrite and cementite in the proportion of seven to one the following relation will indicate the needed amount of combined carbon:

$$\text{Ferrite} = 100 - G - 10Ph - 15C = 7 \times 15C = 105C$$

$$\downarrow$$

$$\text{cementite}$$

$$\text{or } 100 - G - 10Ph - 120C = 0$$

in which G, C, and Ph represent respectively the percentage of graphite, combined carbon, and phosphorus, 15C representing, of course, the proportion of cementite and 10Ph that of steadite.

If the first term of the above equation is greater than 0 the metal will contain free ferrite, i.e. its matrix will be hypo-eutectoid; if it is smaller than 0 it will contain pure cementite, i.e. its matrix will be hyper-eutectoid.

In the presence of 3 per cent of graphite and 1 per cent phosphorus, for instance, the percentage of combined carbon needed to produce a eutectoid matrix will readily be obtained in solving the equation

$$100 - 3 - 10 - 120C = 0$$

which calls for 0.75 per cent combined carbon. Less combined carbon would produce free ferrite while more would cause the formation of free cementite.

In calculating the structural composition of any phosphoretic cast iron of known percentage of phosphorus, graphite, and combined carbon, it should first be ascertained therefore whether its matrix will be hypo- or hyper-eutectoid. Let us assume, for instance, a cast iron containing 1.50 per cent phosphorus, 3.25 per cent graphite, and 0.40 per cent combined carbon. Since $100 - 3.25 - 15 - 120 \times 0.40$ is greater than 0 the matrix of the iron will be hypo-eutectoid, that is the metal will contain free ferrite. The following equations will then permit the ready calculation of its structural composition.

(1) $P + F + S + G = 100$
(2) $P = 120C$
(3) $S = 10Ph$

which give

Pearlite (P)	= 48.00	per cent
Free ferrite (F)	= 33.75	" "
Steadite (S)	= 15.00	" "
Graphite (G)	= 3.25	" "
	100.00	

Taking another example, a cast iron containing 2 per cent graphite, 1.50 per cent combined carbon, and 0.75 per cent of phosphorus, since $100 - 2 - 7.50 - 120 \times 1.50$ is less than 0, the iron will contain free cementite. Its structural composition will be obtained by solving the equations

$$(1)\ P + Cm + S + G = 100$$
$$(2)\ P = \tfrac{8}{7}\ (100 - 15C - 10Ph - G)$$
$$(3)\ S = 10Ph$$

which give

Pearlite (P)	= 77.78 per cent
Free cementite (Cm)	= 12.72 " "
Steadite (S)	= 7.50 " "
Graphite (G)	= 2.00 " "
	100.00

Chemical vs. Structural Composition. — It will now be instructive to compare the chemical composition of cast iron both ultimate and proximate with its structural composition. To that effect let us assume a cast iron of the following ultimate chemical composition:

Graphitic carbon	3.00 per cent
Combined carbon	0.50 " "
Silicon	2.00 " "
Phosphorus	1.50 " "
Manganese	0.40 " "
Sulphur	0.02 " "
Iron (by difference)	92.58 " "
	100.00

In view of the foregoing considerations the following proximate compounds will be formed:

(1) 0.02 per cent S will produce about 0.05 per cent MnS.
(2) 0.05 per cent MnS contains about 0.03 per cent Mn.
(3) This leaves 0.40 − 0.03 = 0.37 per cent Mn in excess to combine with carbon.
(4) 0.37 per cent Mn will form 0.39 per cent Mn_3C.
(5) 0.39 per cent Mn contains about 0.02 per cent carbon.
(6) This leaves 0.50 − 0.02 = 0.48 per cent carbon to combine with iron.
(7) 0.48 per cent carbon will form 7.20 per cent Fe_3C.
(8) 1.50 per cent phosphorus will form 9.63 per cent Fe_3P.
(9) 2.00 per cent silicon will form 6 per cent FeSi.

The proximate chemical analysis of the cast iron considered will consequently be:

Graphitic carbon	3.00 per cent
Fe_3C	7.20 " "
Mn_3C	0.39 " "
Fe_3P	9.63 " "
FeSi	6.00 " "
MnS	0.05 " "
Iron (by difference)	73.73 " "
	100.00

Knowing the proximate chemical constituents the structural composition can be readily calculated. The Fe_3C and Mn_3C form the cementite, hence the cast iron contains 7.20 + 0.39 = 7.59 per cent cementite. The whole of this cementite, since the iron evidently has an hypo-eutectoid matrix, will combine with ferrite in the proportion of 7 to 1 to form pearlite, hence the cast iron will contain 7.59 × 8 = 60.72 per cent pearlite; 1.50 per cent phosphorus means 15 per cent of steadite; the 6.00 per cent of FeSi will be dissolved in the ferrite while the small quantity of MnS will occur as independent minute particles. The structural composition will therefore be:

Pearlite (P)	= 60.72 per cent
Free ferrite (F) (by difference)	= 21.23 " "
Steadite (S)	= 15.00 " "
Graphite (G)	= 3.00 " "
MnS	= 0.05 " "
	100.00

The quicker method for the calculation of the structural composition of cast iron given in foregoing pages, and in which the presence of manganese, silicon, and sulphur is ignored would have given:

Pearlite (P)	60.00
Free ferrite (F)	22.00
Steadite (S)	15.00
Graphite (G)	3.00
	100.00

For practical purposes these values are identical to those obtained from a knowledge of the complete analysis of the iron.

Experiments

Samples of gray cast iron having respectively hypo- and hyper-eutectoid matrix as well as a sample of white cast iron should be prepared for microscopical examination. They should be examined both before and after etching. In the unetched condition the graphite plates will stand out sharply on a brilliant, white background. After etching the following features should be noted, (1) the polyhedric character of the ferrite grains in cast iron containing a small amount of combined carbon, (2) the increasing proportions of pearlite in cast iron with hypo-eutectoid matrix as the percentage of combined carbon increases, (3) the laminations of the pearlite areas, (4) the occurrence of free cementite in cast iron containing more than some 0.80 per cent combined carbon and (5) the occurrence of phosphide eutectic (steadite) in all cast irons containing an appreciable proportion of phosphorus.

The samples should be photographed under a magnification not exceeding 100 diameters.

Examination

I. Explain the occurrence of phosphorus in cast iron.

II. A cast iron contains 2.50 per cent graphite, 0.75 per cent combined carbon, and 1.25 per cent phosphorus. Will its matrix be hypo- or hyper-eutectoid? Explain your answer.

III. What will be (1) the proximate chemical composition and (2) the structural composition of a cast iron having the following chemical ultimate composition:

Graphitic carbon	2.50 per cent
Combined carbon	1.00 " "
Silicon	1.50 " "
Phosphorus	1.25 " "
Manganese	0.50 " "
Sulphur	0.04 " "
Iron (by difference)	93.21 " "
	100.00

LESSON XXI

MALLEABLE CAST IRON

Graphitizing of Cementite. — The unstability of cementite has already been alluded to. It has been mentioned that the prolonged annealing of high carbon steel above its critical range was always likely to result in the formation of some graphitic carbon through the dissociation of the unstable cementite according to the reaction:

$$Fe_3C = 3Fe + C$$

The graphitic carbon formed in this way is often called, according to Ledebur, "temper" carbon to distinguish it from the graphite formed during the solidification of cast iron. This breaking up of cementite into ferrite and graphite takes place the more readily (1) the more combined carbon in the metal, (2) the higher the temperature, (3) the longer the exposure to a high temperature, (4) the more silicon and the less manganese and sulphur present. The influence of a large amount of combined carbon in promoting the graphitizing of cementite is made evident by the facts (1) that iron-carbon alloys containing less than some 0.50 per cent carbon cannot be made graphitic under the most favorable annealing conditions even when containing much silicon, (2) that in steel containing in the vicinity of one per cent carbon the graphitizing proceeds very slowly and remains partial, and (3) that in alloys containing 2.50 per cent or more of combined carbon and a sufficient amount of silicon the conversion of cementite into iron and graphite takes place readily and can be carried to completion, combined carbon disappearing altogether. The influence of temperature and time upon the dissociation of cementite was to be expected. Evidences will be presented in Lesson XXIII to show that the higher the temperature at which cementite forms the more readily is it converted into iron and graphitic carbon during solidification and subsequent cooling. The influence of silicon in graphitizing cementite could likewise have been anticipated because of its well-known power to cause the formation of graphitic carbon during and below solidification. It will be argued in Lesson XXIII that the formation of graphite during solidification always results from the dissociation of cementite, that is, that cementite (Fe_3C) always forms first but being very unstable readily breaks up into iron and graphite, its dissociation being promoted (1) by slow cooling and (2) by the presence of silicon.

The conversion of combined carbon into graphitic or rather temper carbon finds an important industrial application in the manufacture of so-called malleable cast-iron castings, also termed "malleable castings," "malleable cast iron," and even "malleable" pronounced "mallable."

The metallography of these castings should now be considered.

Malleable Cast-Iron Castings. — The adjective "malleable" always used in describing these castings is misleading for it suggests a malleability, and other properties akin to those of steels, which malleable castings are far from possessing. By malleability the metallurgist always understands that property which makes it pos-

sible to convert a metallic mass into commercial shapes by rolling, hammering, etc., and such degree of malleability is not present in malleable cast iron. It is why in the author's opinion this product should continue to be classified as cast iron in spite of the arguments recently presented to classify it as steel on the ground that it is more malleable than ordinary cast iron. The manufacture of malleable cast-iron castings consists in subjecting to a long annealing treatment cast-iron castings of suitable composition whereby some of the carbon may be expelled by oxidation while most if not the whole of the remaining is converted into graphite (temper carbon). The various factors influencing this operation will be briefly described.

Original Castings. — The castings to be subjected to the malleablizing treatment are often called "hard" castings because they are invariably made of white cast iron and are therefore very hard and brittle. The reason why the original castings must be made of white cast iron will be obvious if it be considered that the malleability to be imparted to these castings is to result chiefly, and in some cases altogether, from a conversion of combined carbon into temper carbon as explained above. Any graphite particle existing in the casting will be unaffected by the annealing treatment and will be a source of weakness in the finished casting. Clearly, therefore, the hard castings should be free from graphitic carbon. As to the amount of carbon that should be present, theoretical considerations lead us to conclude that the less carbon the more ductile should be the casting after thorough malleablizing, for, after all, the particles of temper carbon while much less injurious than the hard brittle cementite from which they are derived are nevertheless a source of weakness chiefly because of their breaking up the continuity of the metallic mass. Again a smaller proportion of carbon necessarily means a shorter annealing operation. The desirability of low carbon content in cast-iron castings to be malleablized is universally recognized and it is partly why a large proportion of these castings are made in the "air" furnace, as by its use the percentage of carbon can be lowered. On the other hand, as already mentioned, if the proportion of combined carbon be small the graphitizing takes place with greater difficulty. These considerations point to the existence of a lower as well as of an upper limit for the carbon content of hard castings. In the majority of cases the percentage of carbon varies between 2.50 and 3.00 per cent.

The beneficial action of silicon has been referred to; it greatly promotes the graphitizing of the cementite. It might seem then as if the more silicon in the hard casting the better at least up to some 2 or 3 per cent. Castings of white cast iron cannot be made, however, in the presence of much silicon since this element would cause the formation of graphitic carbon on solidification, even during quick cooling, and the casting would not be white. And since large castings will solidify more slowly than smaller ones it is evident that in large castings especially but a relatively small amount of silicon can be allowed. It is probably true that as much silicon should be introduced in the cast iron as will permit the making of white castings and this proportion of silicon will necessarily decrease as the size of the casting increases. In practise it is found to vary between 0.30 per cent in large castings (one inch thick or more) and 1.25 per cent in very small castings for like solidification conditions and subsequent cooling. In the majority of cases the silicon content varies between 0.50 and 1 per cent.

In Moldenke's opinion the manganese should not exceed 0.60 per cent as a larger amount is liable to cause trouble on annealing and difficulty in machining. Phosphorus according to the same authority should not exceed 0.225 per cent while sulphur should not exceed 0.07 and preferably not 0.05 per cent. These figures represent

American practise only, in Europe cast-iron castings being malleablized containing considerably more sulphur and phosphorus.

The structure of a hard casting of suitable composition for the malleablizing process is shown in Figure 1. It will be seen to be characteristic of the structure of white cast iron.

Annealing Operation. — The hard castings are placed in an annealing box and firmly packed in a suitable material. The boxes are then placed in the annealing furnaces and with their contents exposed to a desirable temperature for a suitable length of time. These various steps should be briefly considered.

Packing Materials. — The packing material affords a support for the castings while it may or may not play an important part in the process itself according to its being (1) oxidizing or (2) non-oxidizing. In his pioneer work, in 1722, Réaumur surrounded white cast iron with crushed iron oxide, the oxygen of which removed a

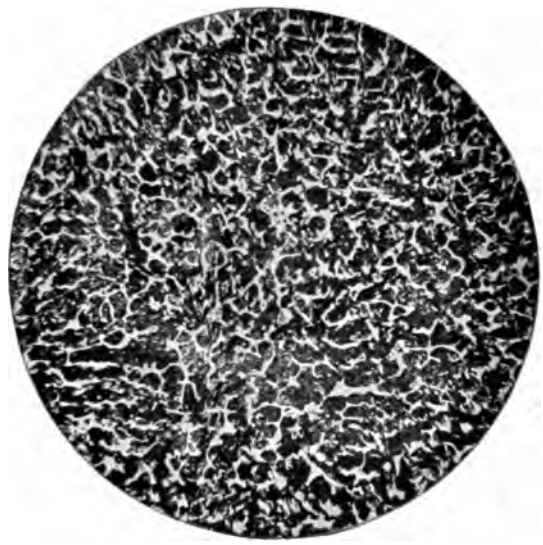

Fig. 1. — Hard casting (white cast iron). Magnified 67 diameters. (Boylston.)

large proportion of the carbon during the subsequent long annealing treatment at a high temperature. Given a sufficiently high temperature and sufficiently long exposure nearly the whole of the carbon could in this way be eliminated from small castings, a small amount of it only remaining as temper carbon. It will be evident that in the operation conducted in this way the oxidizing action of the packing is of more importance in producing malleability than the graphitizing of the cementite. The elimination of the carbon takes place through the well-known reaction between the iron oxide (from the packing) and the carbon in the steel,

$$Fe_3C + 3O = 3Fe + 3CO$$

the cementite in the center migrating towards the outside and being in turn acted upon by the oxygen of the packing material.

It will be evident that this elimination must necessarily proceed from the outside to the center, so that if one should interrupt the operation after a relatively short time he would find an increasing proportion of carbon from shell to center. The use

of an oxidizing and therefore chemically active packing material was for a long time considered essential in the malleablizing process. Later investigations, however, showed that white cast iron could be made malleable solely through the conversion of combined into graphitic carbon with very little if any removal of the carbon and that an oxidizing packing was not therefore necessary. Inert packing such as sand and clay may be used and satisfactory malleable castings produced. It is customary, however, in American practise, to use oxidizing packings but to depend chiefly on the graphitizing of cementite brought about by annealing for the desired malleability and strength. Although realizing that an oxidizing substance as a packing material is not indispensable it is still preferred because of the apparent greater strength its use confers to the castings. The substances most used are powdered iron oxides in the shape of iron ore, mill scale, "bull-dog," etc., and, according to Moldenke, the crushed flakes detached from the annealing pots themselves.

Annealing for Malleablizing. — The malleability imparted to white cast iron by annealing results from, as explained in the foregoing pages, (1) the hard brittle cementite being converted into minute rounded particles of soft graphitic (temper) carbon and (2) the burning of some carbon by the oxygen of the packing materials. If we depend chiefly upon the burning of the carbon for the desired malleability, so-called "white heart" castings are produced, while if the graphitizing of cementite is mainly sought, so-called "black heart" castings are obtained. The temperature and length of the annealing operation vary according to the kind of castings wanted.

The annealing operation is always conducted above the critical point $Ac_{3\cdot2\cdot1}$ of the white cast iron and of course below its solidification, that is when the metal exists as an aggregate of cementite and solid solution (saturated austenite) as explained in Lesson XXIII. It is not known whether the free or the dissolved cementite is graphitized first or whether the dissociation of both kinds proceeds simultaneously. Noting, however, that the graphitizing takes place more readily in the presence of a considerable quantity of combined carbon and, therefore, of free cementite, whereas in the presence of but little free cementite (cast iron with less than 2 per cent carbon) it is at best very slow and remains partial, it seems logical to infer that it is the free cementite which is first decomposed, indeed that its presence is necessary to cause the graphitizing of the dissolved cementite.

Annealing for "White Heart" Castings. — In the making of white heart castings a very large proportion of the carbon is removed by oxidation through the use (1) of an oxidizing packing, (2) of a high annealing temperature, and (3) of a long annealing. The original malleable castings made by Réaumur were of this type and his method is still the prevailing one in Europe. The castings are annealed for four or five days at a temperature of 800 to 900 deg. C. By removing some castings from the annealing box from time to time and examining their structure the progress of the operation may be readily observed. The following transformations are noted as the operation progresses: (1) a narrow white rim of decarburized metal caused by the burning of the carbon from the outside of the casting and a dark center caused by the graphitizing of some of the cementite, (2) a broader white rim and a smaller and darker core due to the burning of more carbon and to the formation in the center of the casting of more graphitic carbon, the graphitizing of the cementite being now indeed possibly complete, (3) the fracture of the metal is now white and steely to the very center showing that most of the carbon has been removed by oxidation. These conclusions are fully confirmed by the microscopical examination of the structure of castings subjected to this annealing treatment for various lengths of time. As this oxidation

of the carbon is necessarily a very slow process, white heart castings of small size only are made, generally not over ½ inch thick. For malleablizing larger castings the "black heart" process soon to be described is decidedly superior.

White heart castings have a rather coarse fracture and structure because of the high and prolonged heating to which they were exposed. Since they resemble low carbon steels in composition and structure it would seem as if their properties could be very materially improved by suitable heat treatment as, for instance, by annealing followed by cooling in oil or in air according to their carbon content. Moldenke states that the European white heart malleable castings bend excellently and are very good, though slightly weaker than black heart castings.

Annealing for "Black Heart" Castings. — For the production of black heart castings, since the oxidation of carbon is of secondary importance, the annealing temperature needs not be so high nor indeed is it necessary to use an oxidizing packing. As already mentioned, oxidizing packings are generally used, however, because of the apparent greater strength they impart to the castings. A certain amount of carbon, therefore, is burnt at the surface of the casting causing a narrow white rim while the core is very dark, hence the name of black heart given to these castings. This darkness of the core is due as we now understand it to the transformation of cement carbon into temper carbon.

The annealing temperature for the production of black heart castings is generally between 750 and 800 deg. C. in the case of air furnace iron, that is, but slightly above the critical range of the metal and the length of time at the full converting temperature between 2½ and 3 days. Moldenke states that cupola iron castings should be annealed at temperatures some 65 to 120 deg. higher and writes:

"Just why there should be a difference in the temperature required for castings of the same composition when made in the cupola or in the air furnace, is one of the unsolved problems. It may be chemical in that the degree of oxidation has its effect on the opening up of the structure under the influence of heat. It may, on the other hand, be a matter of molecular physics, and depend on the constitution and structure of the castings as made, either in the contact of fuel with iron, or not. Possibly it may be a combination of both the chemical and the physical. Yet the problem still remains to be solved."

In completely malleablized black heart castings practically the whole of the carbon should be present in the graphitic condition, the castings consisting then of a narrow case of decarburized iron and of a core made up of ferrite and particles of temper carbon, as shown in Figures 2 and 3. If the malleablizing is but partial because of too low a temperature, too short a treatment, too little silicon, or for some other reason, considerable dissolved carbon may remain which in cooling through the critical range will give rise to the formation of pearlite. The structure of such partially malleablized cast iron is illustrated in Figures 4 to 6. It will be seen to consist of graphitic carbon, pearlite, and ferrite. The mechanism of the formation of such structures is obvious. At the end of the annealing treatment the metal consisted of a mass of austenite in which were embedded a number of particles of temper carbon; on slow cooling through the range the hypo-eutectoid austenite rejected some free ferrite until, its composition reaching the eutectoid carbon ratio, it was converted into pearlite. It will be noted that the pearlitic areas which should indicate the location of the residual austenite are situated away from the temper carbon particles, the latter being surrounded by ferrite.

The annealing of white cast iron may be so incomplete as to retain so much dis-

solved carbon that in slow cooling free cementite as well as pearlite will be formed. This is well shown in Figure 7. In this case the austenite which existed above the

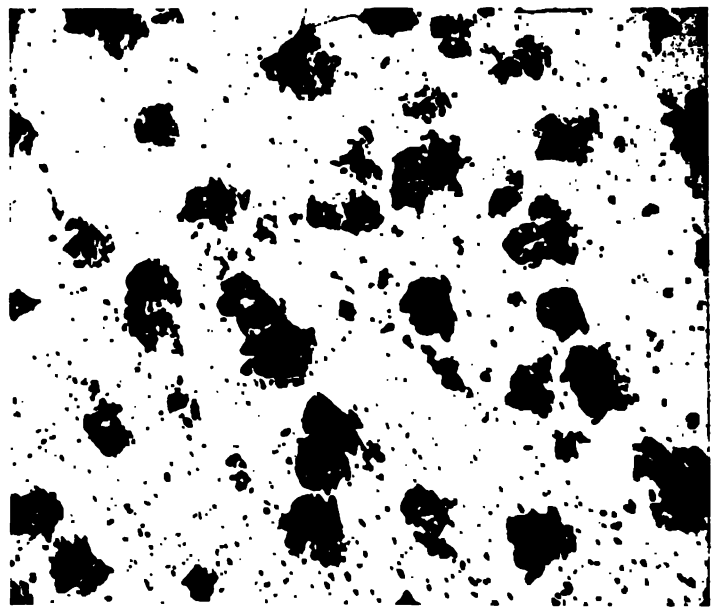

Fig. 2. — Black heart casting. Magnified 100 diameters. Not etched
(F. C. Langenberg in the author's laboratory.)

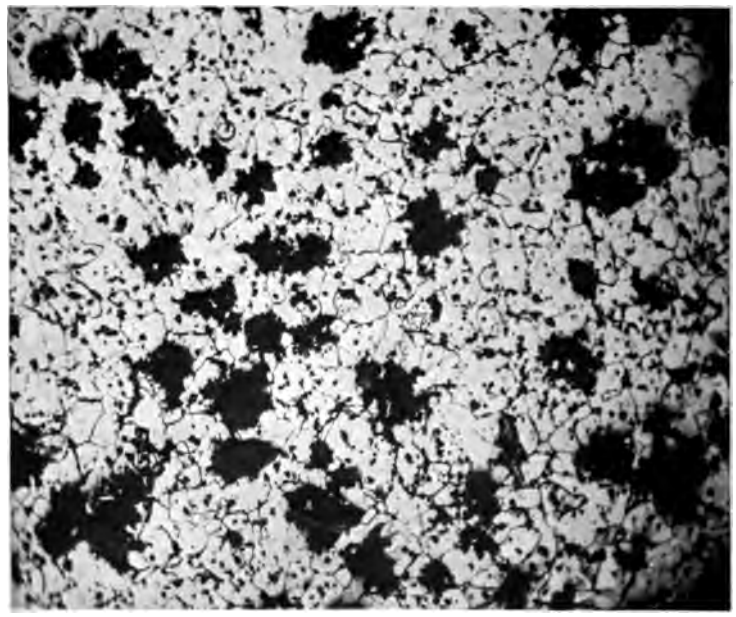

Fig. 3. — Same metal as in Fig. 2. Magnified 100 diameters. Etched
(F. C. Langenberg in the author's laboratory.)

[illegible] at the annealing operation was hyper-eutectoid, that is, it contained [illegible] per cent, or thereabout, of dissolved carbon and on cooling through

the range, therefore, liberated some free cementite. It is evident that partially malleablized cast iron, that is, cast iron still containing considerable combined carbon, cannot be as malleable as malleablized cast iron free from combined carbon since its metallic matrix is necessarily less malleable.

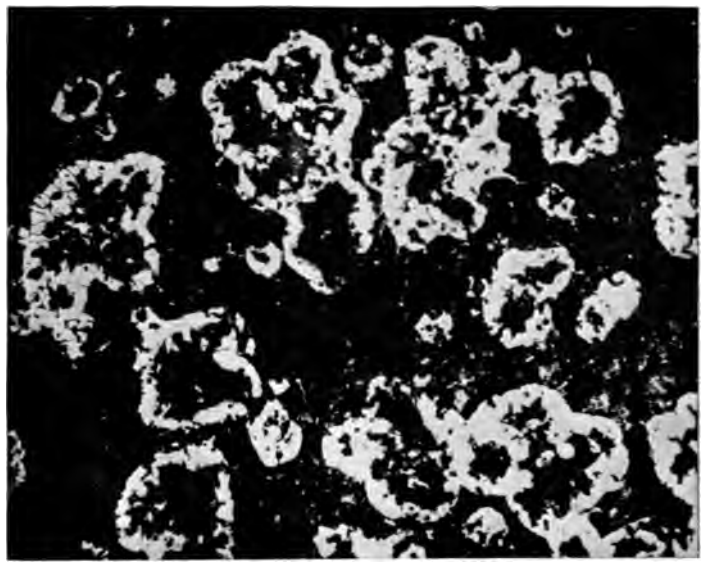

Fig. 4. — White cast iron partially malleablized. Magnified 100 diameters. Particles of temper carbon surrounded by white ferrite. The dark background is pearlite. (F. C. Langenberg in the author's laboratory.)

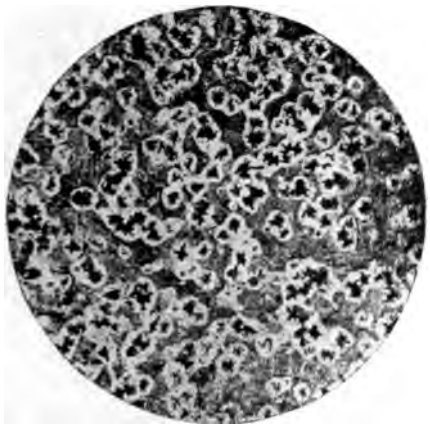

Fig. 5. — White cast iron partially malleablized. Magnified 50 diameters. (Wüst.)

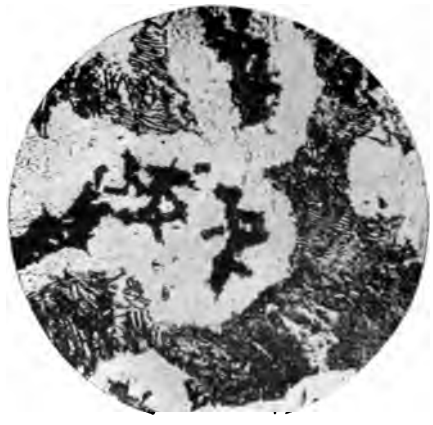

Fig. 6. — Same metal as in Fig. 5. Magnified 500 diameters. (Wüst.)

Gray Cast Iron vs. Malleable Cast Iron. — From the foregoing description of the nature and manufacture of malleable cast-iron castings it is evident that gray cast iron and malleable cast iron may have exactly the same chemical composition, although, of course, the former will generally contain more silicon and total carbon. In spite of identical or nearly identical composition, however, these two metals differ enormously in physical properties, gray cast iron being weak and brittle, malleable cast iron

much stronger, and endowed with remarkable shock-resisting qualities. To account for this we must look into the microstructure of both metals when it will be observed that in gray cast iron the graphite occurs in large, generally curved, flakes and plates whereas in malleable cast iron it is present in small rounded particles, and it may well be conceived that the mode of occurrence of graphite in gray iron breaks up the continuity of the metallic matrix much more effectively, therefore, weakening it and

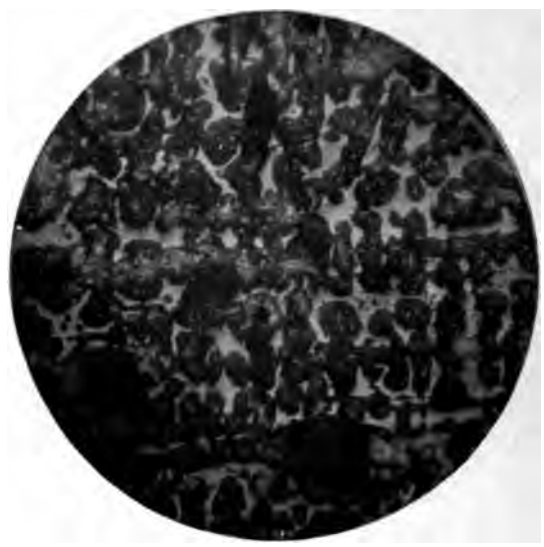

Fig. 7. — White cast iron slightly malleablized. Magnified 100 diameters. (H. F. Miller in the author's laboratory.)

destroying its ductility. Were it possible during the solidification of cast iron to cause the graphite to occur as it does in malleable cast iron, there is no reason to doubt but that it would be as strong and as ductile.

Experiments

Samples of fully and of partially malleablized cast iron should be prepared for microscopical examination as well as a sample of white cast iron suitable for the malleablizing process. They should be examined both before and after etching and their structures compared with the illustrations of this lesson. The following features should be noted: (1) the decarburized shells surrounding the graphitic cores of the malleablized castings, (2) the polyhedric structure of the ferrite of fully malleablized cast iron, (3) the ferrite areas surrounding the temper carbon particles of partially malleablized samples having an hypo-eutectoid matrix, and (4) the occurrence of free cementite in very incompletely malleablized castings.

Examination

I. Explain the graphitizing of cementite.

II. Describe the structure of (1) fully malleablized black heart castings and (2) of partially malleablized black heart castings.

III. Explain the apparent reason for the malleability of annealed white cast iron and the lack of malleability of gray cast iron containing the same proportion of graphitic carbon.

LESSON XXII

CONSTITUTION OF METALLIC ALLOYS

For many years vague and conflicting opinions were entertained in regard to the nature of metallic alloys. It was not known whether these intimate associations of two or more metals were merely mechanical mixtures or chemical compounds while the existence of solid solutions was unsuspected. The application to the study of metallic alloys of the determination of the solubility curves which had proved so fruitful in investigating the mechanism of the solidification of ordinary (liquid) solutions and of mixtures of melted salts, soon followed by the microscopical examination of their structure have at last revealed their true constitution. We know now that metallic alloys may be considered as solution of high freezing (solidification) point and, therefore, solid at ordinary temperature, whereas the old conception of solution applied only to substances liquid at that temperature. It is evident, however, that the location of the freezing-point of a substance in the temperature scale can have no bearing whatever upon its constitution, that is, upon the mode of occurrence of its constituents and the nature of the bond uniting them.

In these lessons the constitution of metallic alloys will be considered only so far as necessary to understand the equilibrium diagram described in Lesson XXIII in which steel and cast iron are considered as alloys of iron and carbon, i.e. as solutions of these elements, liquid at a very high temperature, frozen at ordinary temperature.

Since moreover steel and cast iron are considered as pure iron-carbon alloys it will suffice for our purpose to deal only with alloys of two metals, that is, with binary alloys.

The constitution of alloys is revealed chiefly (1) through the mechanism of their solidification as disclosed by their "fusibility" curves, and (2) through the microscopical examination of their structure after solidification.

Solidification of Pure Metals. — Let us first consider the solidification of a pure metal by observing its rate of cooling from the molten to the solid condition. This involves the use of a pyrometer, preferably a thermo-electric (Le Chatelier) instrument, the hot junction of which, suitably protected, is embedded in the cooling metal. By recording the successive intervals of time in seconds required for each successive cooling through ranges of temperature say of 10 deg. C., and plotting time against temperature a cooling curve of the type shown in Figure 1 is obtained.[1] The teachings of such curves are obvious. Starting with the molten metal at A, its temperature being T, its cooling from A to B, while its temperature is falling from T to Ts is uniformly retarded. This results in the smooth, nearly straight portion AB of the curve. The cooling of a molten metal above its solidification point is in this respect similar to the cooling of any substance free from thermal critical points; the cooling curves

[1] Self-recording pyrometers may also be used.

obtained in such cases are always smooth curves indicating a uniform increase in time as the temperature of the substance falls. The curve of Figure 1 indicates the occurrence of a sharp critical point at the temperature *Ts* corresponding to the horizontal portion *BC* of the curve. It is evident that on reaching *Ts* the temperature of the metal suddenly ceased to fall and remained stationary during an interval of time represented by *tt'*. The metal then resumed a normal rate of cooling which was continued to atmospheric temperature as indicated by the smooth portion *CD* which, were it not for the jog *BC*, would be a continuation of *AB*. We naturally connect this sudden appearance of a critical point in the cooling curve with the solidification of the

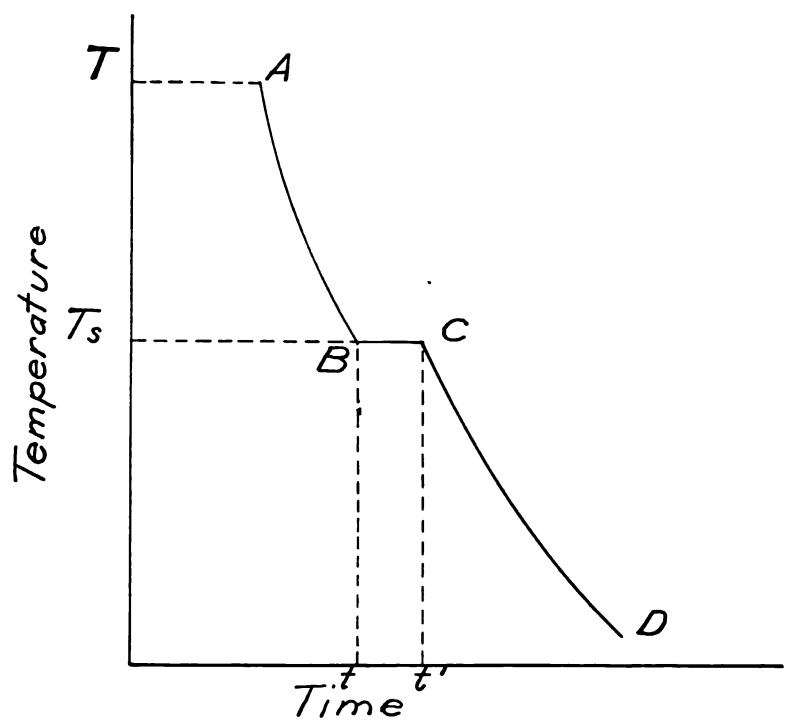

Fig. 1. — Typical cooling curve of pure metal.

metal. It clearly indicates (1) that the metal begins to solidify at the temperature *Ts*, (2) that while it is solidifying its temperature remains constant, (3) that the solidification lasts $t' - t$ seconds. It is evident that during its solidification the metal was exposed to the same cooling influences as those prevailing above and below it, and since its temperature nevertheless remains constant it must be that heat is here liberated in amount exactly sufficient to make up for the heat lost by radiation and conductivity. Any attempt at increasing the rate of cooling during solidification would result in hastening solidification and not in lowering the temperature of the metal. The heat evolved during the solidification of a substance is known as its "latent heat of solidification." In Figure 1, *AB* then represents the cooling of the liquid metal, *BC* its solidification, and *CD* the cooling of the solidified metal. On heating a pure metal from below to above its melting-point, a similar curve is obtained indicating (1) that the melting-point coincides with the solidification point, at least under normal

conditions, and (2) that the melting takes place at a constant temperature, being, therefore, accompanied by an absorption of heat.

In Figure 2 the cooling curves of several pure metals are shown. They differ only in regard to the location of the horizontal portions indicating the temperatures of solidification.

The structure of pure metals has been described in Lesson I, when they were shown to be made up of polyhedral crystalline grains, each grain consisting of true crystals of uniform orientation. As an instance of the structure of pure metals, the structure of pure lead is shown in Figure 3.

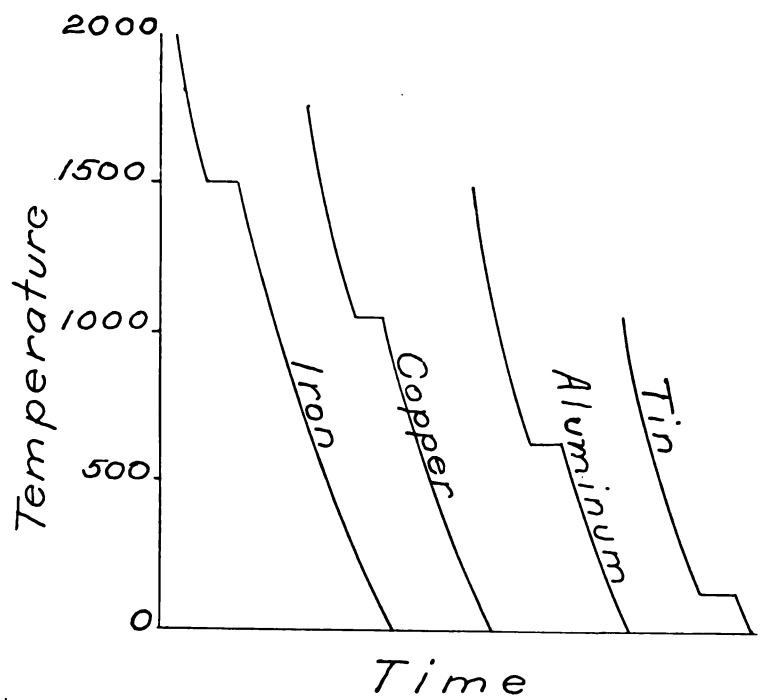

Fig. 2. — Cooling curves of various pure metals.

Solidification of Binary Alloys the Constituents of which Form Solid Solutions. — The cooling or solidification curves of alloys of two or more metals may be constructed exactly like the cooling curve of a pure metal, namely, by observing the rate of cooling as the temperature is lowered from above the melting-point to atmospheric temperature and plotting the intervals of time against the corresponding temperature falls. A number of binary alloys are then found to yield cooling curves of the type shown in Figure 4. From A to B, that is, as the alloy cools from T to Tb, the curve is smooth and, therefore, indicative of normal cooling. At B there is a sudden change of direction and from B to C, that is, from the temperature Tb to the temperature Tc, the cooling of the alloy is evidently abnormally slow. From C to D, that is, from the temperature Tc to atmospheric temperature, the cooling is again normal. Since the portion BC of the curve clearly indicates spontaneous evolutions of heat causing a marked retardation in the cooling of the alloy and lasting $t'-t$ seconds, we naturally infer that it corresponds to its solidification. It follows from the appearance of the cooling curve

that alloys yielding such curves do not, like pure metals, solidify at a constant temperature but that their solidification, on the contrary, lasts $t'-t$ seconds while their temperature falls from *Tb* to *Tc*. Summing up, *AB* indicates the cooling of the molten alloy, *B* the beginning, and *C* the end of its solidification, tt' the time required for its solidification, *Tb Tc* the fall of temperature during solidification, and *CD* the cooling of the solidified alloy. Above the point *B*, therefore, the alloy is entirely liquid, below *C* it is entirely solid, while between *B* and *C* it is partly liquid and partly solid. The point *B* is accordingly called the liquidus point and *C* the solidus point.

Binary alloys whose cooling curves are of the type shown in Figure 4 are known to be solid solutions. In these alloys the component metals which are completely merged in the liquid condition remain likewise so completely merged after solidification that their separate existence cannot be detected by microscopical examination or

Fig. 3. — Pure lead. Magnified 20 diameters. (F. C. Langenberg in the author's laboratory.)

other physical means. They formed, on solidifying, homogeneous crystals containing both metals in indefinite proportions. These crystals are sometimes called "mixed crystals" and substances yielding them "isomorphous" mixtures by which it is meant that only isomorphous substances[1] can yield mixed crystals or in other words can form solid solutions. The expression "solid solution" is much preferable and is now quite universally used.

The mechanism of the formation of solid solutions of two metals should be examined more closely. Let us assume that a certain proportion of the metal *M* of relatively low melting-point is alloyed with, or dissolved in, the metal *M'* of higher melting-point. The metal *M* may be considered as the solute and *M'* as the solvent. It is believed that when solidification begins homogeneous crystals of *M* and *M'* are formed but that they contain a smaller proportion of the fusible metal *M* than the

[1] Isomorphous substances are those that are capable of crystallizing in the same crystallographic forms.

liquid bath, which is thereby enriched in M.[1] On further cooling these crystals grow but the crystalline matter now deposited contains more of the metal M than the crystals first formed, although still less than the molten bath which is further enriched in M and so on, the crystals growing through successive additions of crystalline matter containing increasing proportions of the dissolved and relatively fusible metal M, and approaching, therefore, although not reaching, the composition of the molten metal until finally the last drop solidifies. Meanwhile, as the temperature is lowered through and below the solidification range, diffusion takes place within the crystals so that finally they become chemically homogeneous provided time be given (through slow

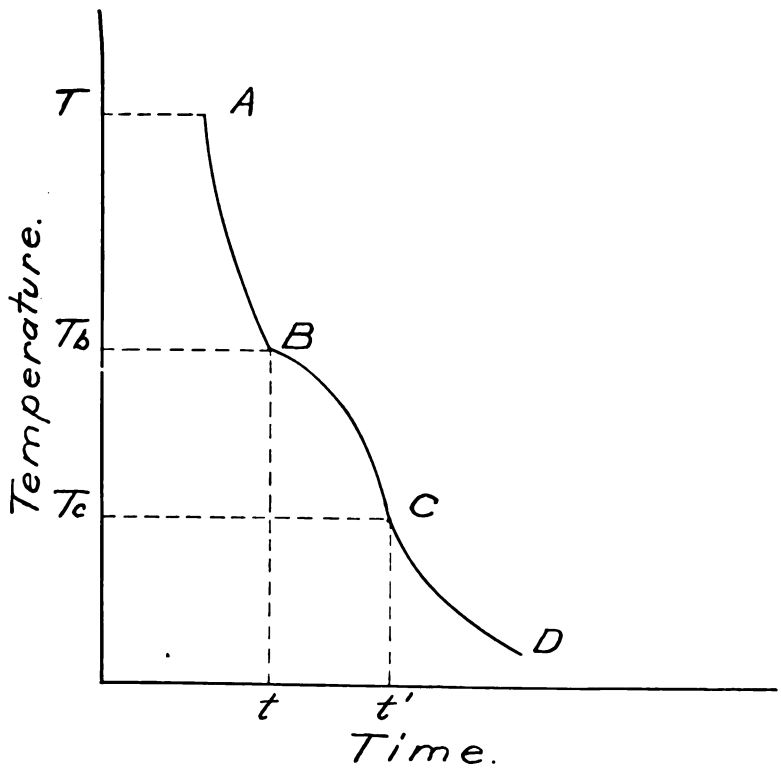

Fig. 4. — Typical cooling curve of binary alloy whose component metals form a solid solution.

cooling) for complete diffusion. Like pure metals, alloys whose component metals form solid solutions, are composed of polyhedral crystalline grains (see Fig. 5).

Fusibility Curves of Binary Alloys whose Component Metals are Completely Soluble in each Other when Solid. — So-called "fusibility curves" or "equilibrium diagrams" are obtained from any series of alloys by constructing the solidification curves, as explained above, of a number of alloys of that series and plotting on a single

[1] It is because the bath becomes richer in the more fusible metal M that its melting-point is lowered, resulting in its solidification covering a considerable and falling range of temperature. If the crystals first formed had the same composition as the bath, solidification would take place at a constant temperature. Witness the solidification of pure metals, of eutectic alloys, and of chemical compounds: the solidifying metal having the same composition as the liquid from which it forms, solidification takes place at a constant temperature.

diagram the evolutions of heat observed. This has been done in Figure 6 by uniting the $BB'B''$ . . . and the $CC'C''$ . . . points denoting respectively the beginning and the end of the solidification of a number of alloys $AA'A''$ . . . Leaving out the independent cooling curves used for the construction of the fusibility curve, the diagram shown in Figure 7 is obtained, the co-ordinates being now temperature and composition. The figure is typical of the fusibility curves of binary alloys whose component metals are entirely soluble in each other when solid. They are composed of two branches, one concave the other convex, uniting the melting-points of the constituent metals. MLM' is known as the liquidus because any alloy of the series above that line is entirely liquid, while MSM' is called the solidus because any alloy below it is entirely solid. Within the area $MLM'SM$ the alloys are partly liquid and partly solid. The solidification of these alloys should be further described with the help of this diagram. Let us assume an alloy the composition of which is represented by the point P in the

Fig. 5. — Copper-zinc alloy. Copper 50 per cent. Magnified 200 diameters. Homogeneous solid solution. (Guillet.)

diagram and containing, therefore, 75 per cent of the low melting-point metal M and 25 per cent of the less fusible metal M'. An alloy of that composition at the temperature T is entirely liquid since its condition is represented by a point situated above the liquidus. As the alloy cools from P to l its temperature falling from T to t, it still remains entirely liquid. At l, temperature t, solidification begins through the formation of crystals whose composition must be represented by the point s at the intersection of the solidus and of a horizontal line through l, for it is evident that the only crystals that can be in equilibrium at the temperature t with the liquid of composition l must have the composition s. To clarify, if the crystals in equilibrium with the liquid l at the temperature t have not the composition s, then they must necessarily contain either more of the metal M' or less of that metal. In other words, their composition may be represented by the point x to the left of s or by the point y to its right. It is evident that the composition of the crystals forming at the temperature t from a liquid of composition l cannot have the composition x since the corresponding point falls within the area $MLM'SM$ and since any point in this area cannot represent the composition of the crystals existing at the corresponding temperature but must

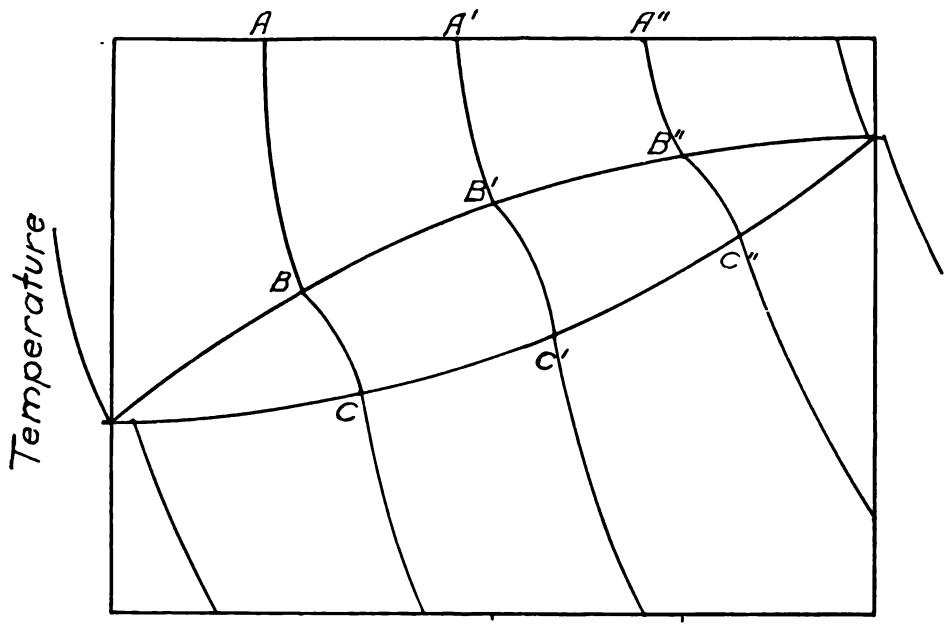

Fig. 6. — Diagram showing how fusibility curves are constructed.

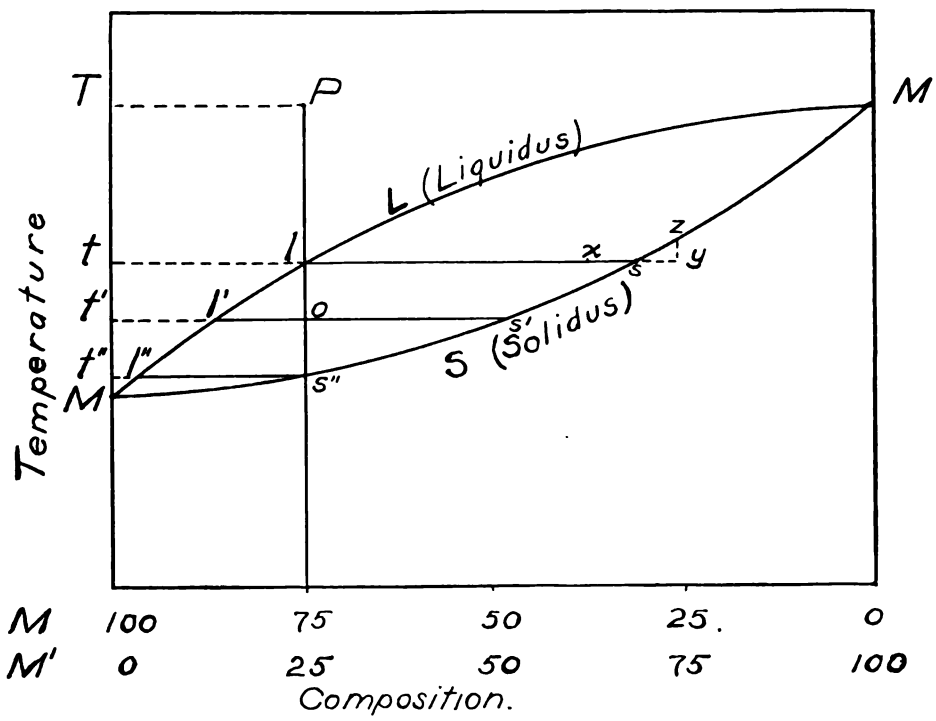

Fig. 7. — Typical fusibility curve of binary alloys whose component metals form solid solution.

represent on the contrary the *average* composition of the partly solidified alloy, hence the crystals forming at t in the case we are considering cannot have a composition represented by a point to the left of s. Assuming the composition of these crystals to

be represented by the point y to the right of s, then it is evident that these crystals must have formed at z, that is, at a temperature considerably higher than t, which cannot be since our alloy does not begin to solidify before the temperature t is reached. Hence the composition of the crystals forming at t, when the alloy P begins to solidify, cannot be represented by a point to the right of s. Clearly the point s must indicate the composition of those crystals. As the alloy cools from l to o, that is, from t to t', the crystals which began to form at l continue to grow by gradual deposition of crystalline matter progressively richer in M while the remaining liquid bath likewise becomes richer in M and consequently more fusible, its varying composition being represented by ll'. For any point o within the area $MLM'SM$, that is, when the alloy is in the process of solidification, the composition of the crystals in equilibrium at the corresponding temperature t' with the solution l' is represented by the point s'. This must

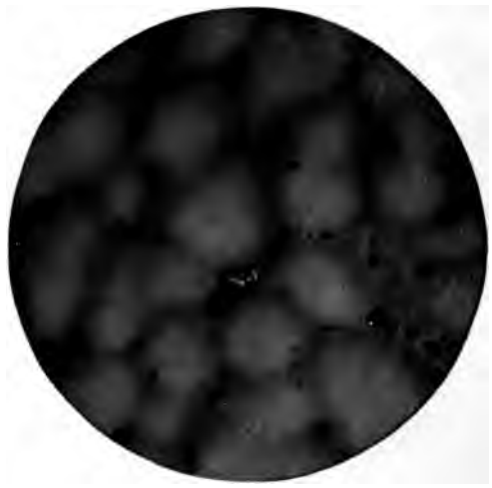

Fig. 8. — Iron-copper alloy. Copper 10 per cent. Magnified 125 diameters. Heterogeneous crystalline grains. The dark parts are richer in copper, the lighter parts richer in iron. (Stead.)

necessarily mean that as the metal cools from t to t' and while the crystals are growing, diffusion must necessarily take place in each crystal so that the concentric layers of varying composition of which we may conceive that they are initially composed, assume the same composition s', the crystals being now homogenous. At s'', temperature t'', the solidification is complete. The last drop of liquid to solidify had the composition l''. By diffusion the crystals, which began to form at s and grew from s to s'', that is, as the temperature fell from t to t'', have assumed a homogenous chemical composition. While this diffusion, however, needed to produce homogenous crystals, readily takes place during the crystallization of liquid solutions, the case is different with solid solutions. Unless solidification and subsequent cooling have been sufficiently slow, solid solutions may remain heterogenous, i.e. the different layers of crystalline matter of which each crystal is composed may not be of identical composition, the proportion of the most fusible metal increasing from center to outside (see Fig. 8). As an instance of binary alloys forming solid solutions the fusibility curve of gold-platinum alloys is reproduced in Figure 9.

Binary Alloys Forming Definite Compounds and Solid Solutions. — When two

metals unite to form solid solutions, it does not necessarily imply that they may not chemically combine with each other as well. Important instances are known of metals forming a definite chemical compound, which compound is then dissolved in the remaining excess metal. Two metals M and M', for instance, may unite chemically to form the compound $MxM'y$ and unless the alloy contains the two metals exactly in the required atomic proportions, the compound may form a solid solution with the excess of metal M or of metal M', as the case may be. In such cases the alloys should be considered not as alloys of two metals but of one metal and of one chemical compound of two metals, when the mechanism described to explain the solidification of solid solutions will be found applicable. Indeed we may conceive the existence of alloys of two metals in which two definite compounds are formed, mutually soluble and, therefore, forming solid solutions. Such alloys should be considered not as alloys

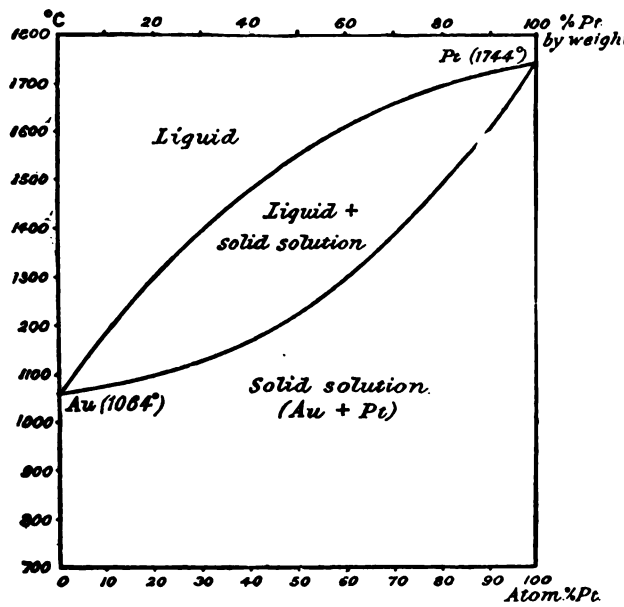

Fig. 9. — Fusibility curve alloys of gold and platinum. (Desch.)

of two pure metals but of two chemical compounds, the mechanism of their solidification being then identical to that of alloys of two metals.

Binary Alloys whose Component Metals are Insoluble in Each Other in the Solid State. — If two metals, although soluble in the liquid state, are insoluble when solid, it is evident that on solidification they must crystallize separately into distinct crystals readily distinguishable under the miscroscope, in other words, that the solid alloy must be an aggregate of the two metals. The study of the mechanism of the solidification of such alloys and of their microstructure should receive some attention.

The typical cooling or solidification curve of an alloy of two metals insoluble in each other when solid is shown in Figure 10. The curves are obtained as previously explained by observing the time required by the alloy to cool through successive and equal ranges of temperature and by plotting the times against the corresponding falls of temperature, or more conveniently and accurately by the use of self-registering pyrometers. The curve of Figure 10 will be seen to consist of four parts, namely, AL

indicating a normal rate of cooling, LL' a retarded cooling, $L'S$ a stationary temperature, and SB a normal rate of cooling to atmospheric temperature. It is logical to infer that AL represents the uniform cooling of the liquid alloy and SB the uneventful cooling of the solid metal, L being the liquidus point, and S the solidus. The portion of the curve $LL'S$ represents the solidification of the alloy as the temperature falls from t to t'. It will be observed (1) that the solidification begins at L, temperature t, (2) that it proceeds from L to L' as the *temperature is falling*, and (3) that the end of the solidification takes place at a *constant temperature*, namely, t', as indicated by the

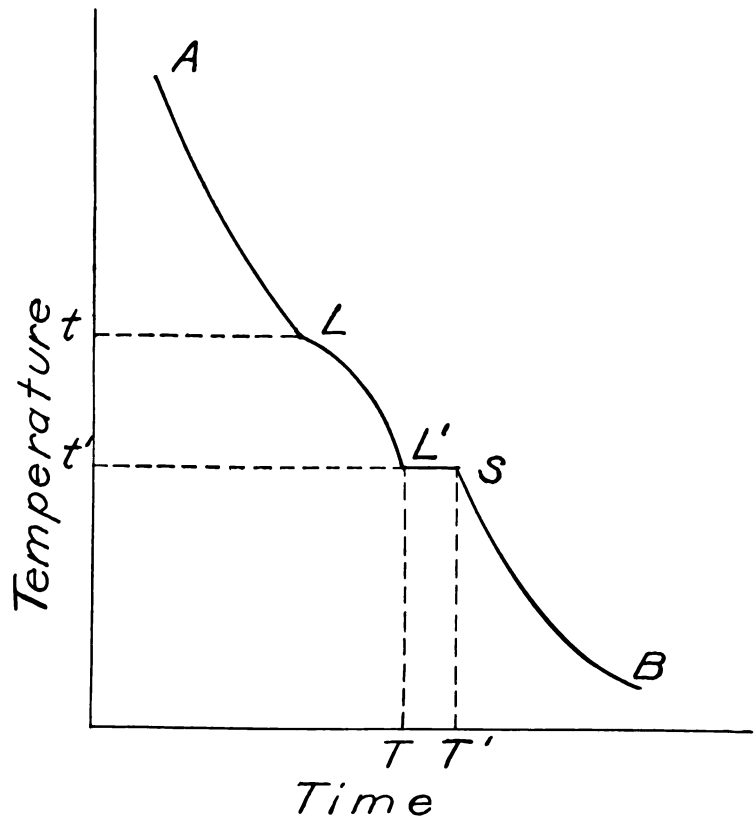

Fig. 10. — Typical cooling curve of binary alloy whose component metals are insoluble in each other in the solid state.

horizontal portion $L'S$, the temperature of the alloy remaining constant during $T'-T$ seconds.

In Figure 11 the solidification curves of a number of alloys of the same series have been constructed as explained above, the alloys arbitrarily selected containing respectively 10, 20, 40, 60, and 80 per cent of metal M. It will be noted that, with the exception of the alloy containing 40 per cent of M, each alloy exhibits two evolutions of heat, namely an upper evolution, L, at varying temperatures and a lower, E, always at the same temperature regardless of the composition of the alloy. By uniting the upper points and the lower ones as indicated by dotted lines in Figure 11, the so-called fusibility curve or equilibrium diagram of that series of alloys is obtained. In Figure 12 the fusibility curve only is represented, the independent cooling curves used for its

construction having been omitted. The co-ordinates are now composition and temperature. The curve indicates clearly the beginning and the end of the solidification

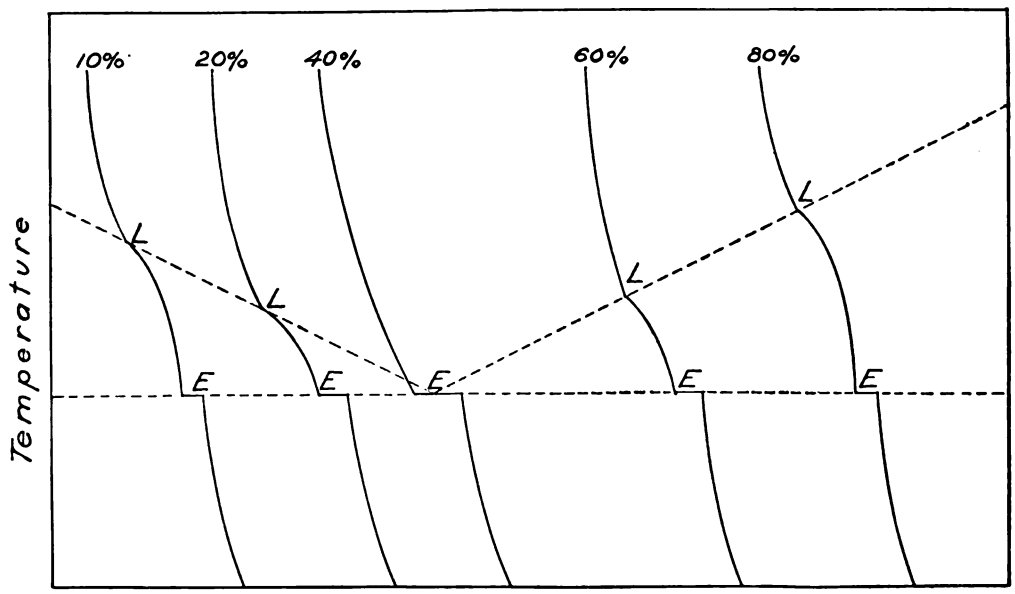

Fig. 11. — Diagram showing how fusibility curves are constructed.

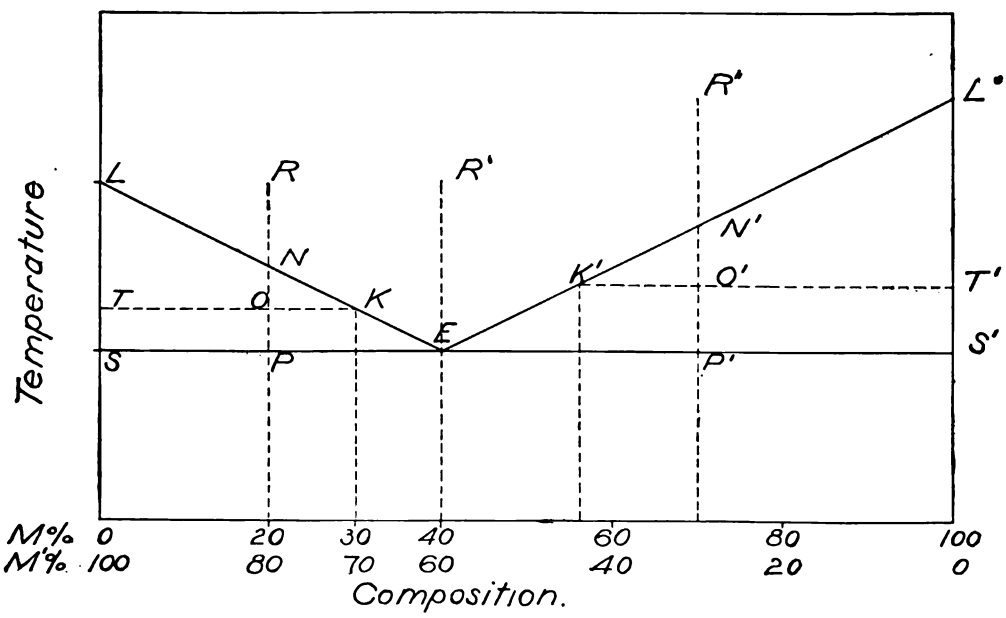

Fig. 12. — Typical fusibility curve of binary alloys whose component metals are insoluble in each other in the solid state.

of any alloy of the series. The solidification of an alloy whose composition corresponds to the point R, for instance, and which, therefore, contains 20 per cent of metal M and 80 per cent of metal M' evidently begins at N and ends at P. The fusibility curve is

made up of three branches, namely, the two intersecting lines LE and $L'E$ starting respectively from the melting-points of the two constituent metals and a horizontal line SS' passing by the point of intersection E of the first two. This is the typical fusibility curve of binary alloys whose component metals are insoluble in each other in the solid condition. The solidification of these alloys should now be examined more closely. Several features are obvious. The different alloys *begin* to solidify at different temperatures according to their composition. At first, as the percentage of M increases from 0 to 40 (a proportion arbitrarily selected), the solidification point is lowered from L to E, while with further increase of M from 40 to 100 per cent, the solidification point is raised from E to L'. The solidification of all alloys, however, *ends* at the same temperature, namely, at the temperature S. Clearly, LEL' is the liquidus and SES' the solidus. The alloy containing 40 per cent of M is evidently the most fusible alloy of the series since it remains liquid until the temperature S is reached while other alloys begin to solidify at higher temperatures. This alloy of lowest melting-point is known as the "eutectic" alloy, from the Greek meaning "well melting." It is evident that, like pure metals, eutectic alloys solidify at a constant temperature, namely the eutectic temperature. Many aqueous solutions also give rise to the formation of solutions of lowest freezing-points called "cryohydrates" and which were at first supposed to be true chemical compounds, that is, hydrates containing salt and water molecules in atomic proportions. And, likewise, eutectic alloys were at first supposed to be definite chemical compounds of the two metals. They are now known to be aggregates of these metals generally very finely divided. This will be made clear by following the solidifications of three alloys, R, R', and R'' (Fig. 12). The alloy R contains, according to the diagram, 20 per cent of the metal M and 80 per cent of the metal M'. Since it contains less of the metal M than the eutectic alloy, we may for convenience refer to it as an hypo-eutectic alloy, although of course in regard to the content of M' it would be hyper-eutectic. In cooling from R to N the alloy remains liquid. At N solidification begins through the formation of pure crystals of M', that is, of the metal which is present in excess above the eutectic ratio. The formation of pure crystals of M' continues as the alloy cools from N to P and meanwhile the portion of the alloy remaining liquid (we may call it the mother metal) becomes gradually richer in M, i.e. it approaches gradually the composition of the eutectic alloy. Finally at P, temperature S, the remaining liquid has exactly the eutectic composition and now solidifies at a constant temperature, the solidification temperature of the eutectic alloy. In other words, as the alloy cools from N to P with formation of pure crystals of metal M' the composition of the portion of the alloy remaining liquid varies according to the line NKE, reaching the composition E, that is, the eutectic composition, always at the same temperature regardless of the initial composition of the alloy. When the alloy has cooled to O, for instance, a point between LE and SE, it is partly liquid and partly solid, its temperature is T and the composition of the liquid portion is represented by K, that is, it contains 30 per cent of the metal M. On further cooling from O to P the composition of the mother metal shifts from K to E.

In the case of the alloy R'', containing a larger proportion of the metal M than the eutectic alloy and which we may, therefore, consider to be hyper-eutectic, when it reaches the point N' its solidification begins, pure crystals of the metal M being formed while the molten bath becomes gradually richer in M' gradually approaching, therefore, the composition of the eutectic alloy, until at the temperature S that composition is reached when the remaining liquid solidifies at a constant temperature.

Any point O' situated between $L'E$ and $S'E$ indicates an alloy in part solid and in part liquid; its temperature is T' and the composition of the liquid is represented by K'. On cooling from O' to P' additional crystals of pure M are formed, or those already formed continue to grow while the composition of the molten metal shifts from K' to E.

Starting with the alloy R' of eutectic composition, it remains liquid until at E, temperature S, it solidifies at a constant temperature, there being no excess metal to be rejected.

Seeing that the branch LE corresponds to the formation of pure crystals of the metal M' and the branch $L'E$ to the formation of pure crystals of the metal M, the conclusion seems irresistible that their point of intersection E must correspond to the

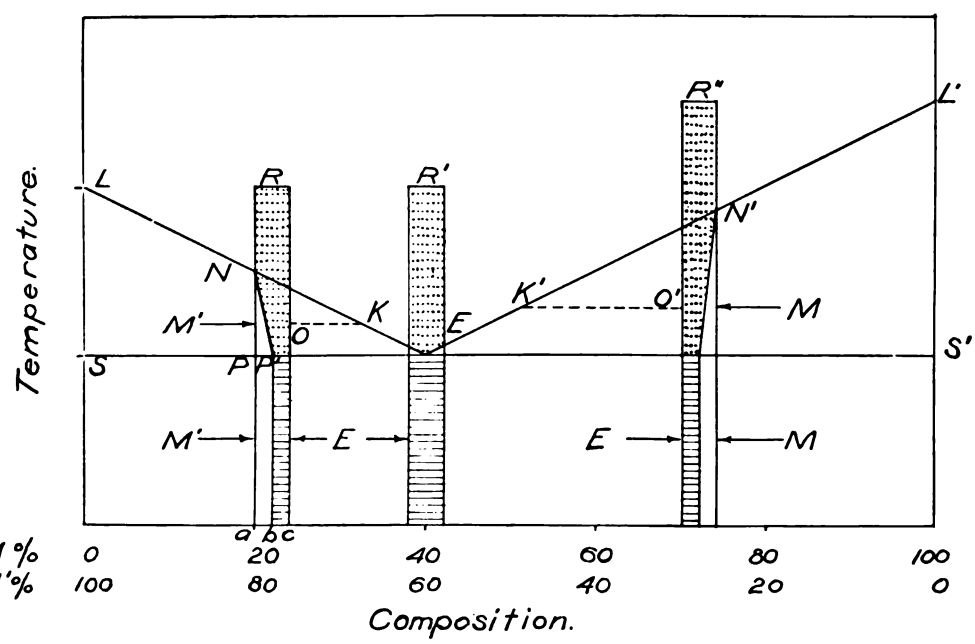

Fig. 13. — Diagram depicting the mechanism of the solidification of alloys whose component metals are insoluble in each other in the solid state.

simultaneous formation of crystals of metal M and of metal M' and that the eutectic alloy, therefore, must be a finely divided aggregate of M and M'. In other words, at any point on the branch LE, the alloy is saturated with the metal M' so that the lowering of its temperature must cause the separation of M' crystals with corresponding lowering of the saturation point, that is, of the solidification point of the bath. In a similar way, at any point on the branch $L'E$, the alloy is saturated with M and a fall in its temperature must result in the formation of M crystals while the solidification point of the portion remaining liquid is thereby lowered. At E the alloy is saturated with both metals so that any attempt at lowering its temperature must result in the simultaneous deposition of crystals of M and of M', and since the composition of the bath remains the same, solidification now takes place at a constant temperature. Hence the constitution of eutectic alloys and the reason for their constant freezing temperature.

It has been attempted in Figure 13, to depict graphically the mechanism of the

solidification of hypo-eutectic, eutectic, and hyper-eutectic alloys. As diagrams of this kind have already been used in these lessons the present one will be readily understood.

When the alloy R, for instance, reaches the point N, crystals of M' form, their

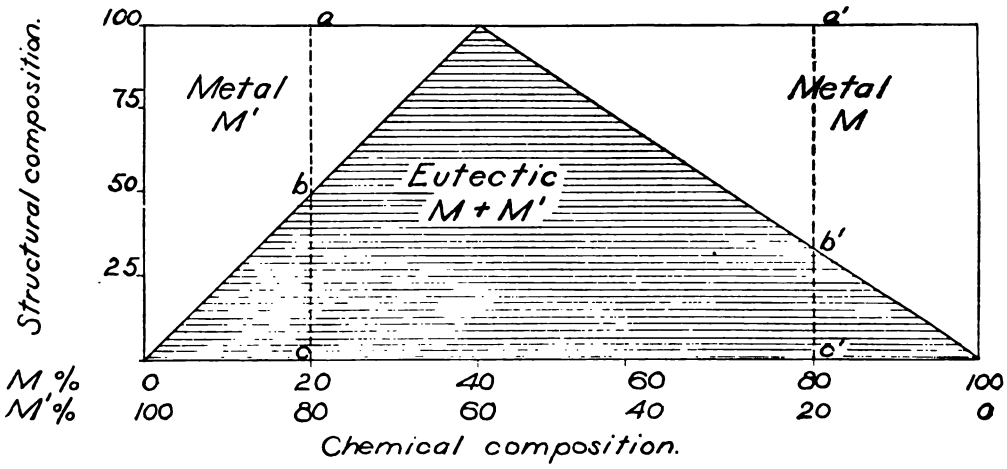

Fig. 14. — Diagram showing the structural composition of binary alloys whose component metals are insoluble in each other in the solid state.

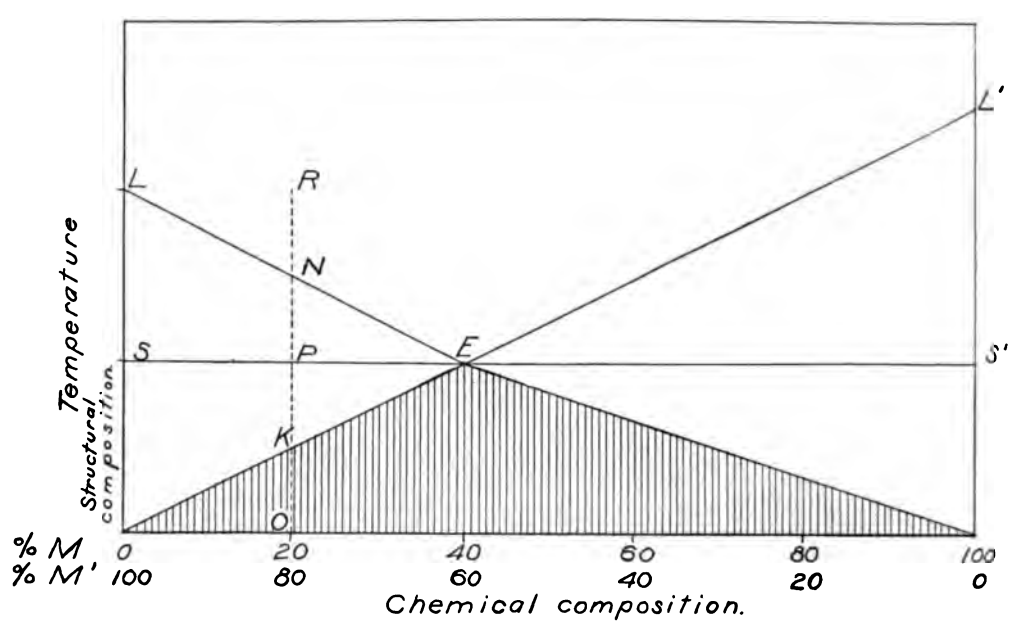

Fig. 15. — Diagram showing the fusibility curve and the structural composition of binary alloys whose component metals are insoluble in each other in the solid state.

formation as the metal cools from N to P being represented by the area NPP'. At P the residual liquid, now of eutectic composition, solidifies at a constant temperature. At any point O the composition of the portion still liquid is represented by K. The completely solidified metal will be made up of ab per cent of metal M and bc per cent of eutectic alloy.

It will not be necessary to describe at greater length the graphical representation of the solidification of the alloys R' and R''.

The structural composition of alloys of two metals completely insoluble in each other in the solid condition may conveniently be represented graphically as shown in Figure

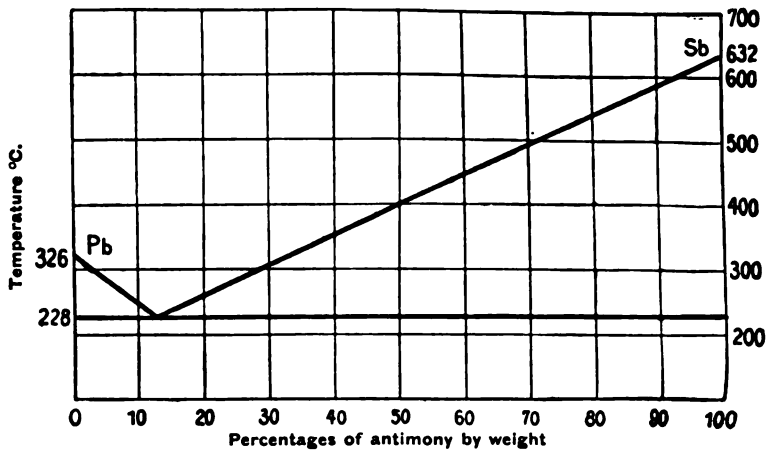

Fig. 16. — Fusibility curve of alloys of lead and antimony. (Roland-Gosselin.)

Fig. 17. — Typical structures of alloys whose compo are insoluble in each other in the solid state. *x*, e *M'* and eutectic; *y*, eutectic; *z*, excess metal *M* a (Gulliver.)

14. The interpretation of this diagram is obvious. An of the metal M, for instance, will be made up of ab per cent tectic alloy. With 40 per cent of M the alloy is wholly of e 80 per cent of M, for instance, it contains $a'b'$ of M cryst

20 per cent
r cent of eu-
while with
of eutectic

The composition diagram may with advantage be combined with the equilibrium diagram as it has been done in Figure 15. Taking an alloy whose composition is represented by R, for instance (20 per cent M and 80 per cent M'), it is seen (1) that it begins to solidify at N, (2) that as it cools from N to P pure crystals of M' are formed, (3) that the percentage of M' thus liberated is represented by PK, (4) that at P the remaining molten alloy now of eutectic composition solidifies, and (5) that KO represents the percentage of this eutectic alloy.

The graphical method used in these lessons for representing the structural composition of alloys was first suggested by the author in 1896. It has since been widely used and Tammann employs it to represent the heat liberated by the solidification of the eutectic or the time taken for its solidification, it being evident that both heat and time must necessarily be proportional to the *amount* of eutectic alloy formed. In

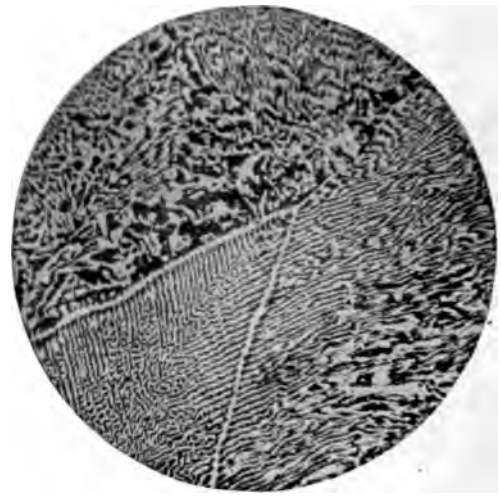

Fig. 18. — Eutectic alloy of bismuth and tin.
Magnified 200 diameters. (Desch.)

Figure 15, therefore, the vertical distances of the shaded area are proportional to the times during which the temperature of the alloys remained constant while the residual baths of eutectic composition were solidifying. The fusibility curve of lead-antimony alloys is reproduced in Figure 16 as an instance of alloys whose component metals are entirely insoluble in each other after solidification.

From the foregoing it appears that solidified alloys of two metals insoluble in each other are aggregates of these two metals and that three types of structure are to be expected (1) the structure of hypo-eutectic alloys composed of crystals or crystalline grains or particles of one metal embedded in, or surrounded by, some eutectic alloy, (2) the structure of hyper-eutectic alloys consisting of crystalline particles of the other metal and of eutectic alloy, and (3) the structure of eutectic alloys consisting of a finely divided aggregate of minute particles of both metals. These three types are represented diagramatically in Figure 17. Eutectic alloys are often made up of very thin alternate and parallel plates or lamellæ of each of the two constituents, but in some cases they consist of rounded or elongated particles of one of the constituents embedded in a matrix of the other constituents. The structures of some

eutectic alloys are shown in Figures 18 to 20. It will be noted that the constituents of eutectic alloys are not always pure metals.

Binary Alloys whose Component Metals are Partially Soluble in each Other when Solid. — Metals are seldom absolutely insoluble in each other when solid, each metal

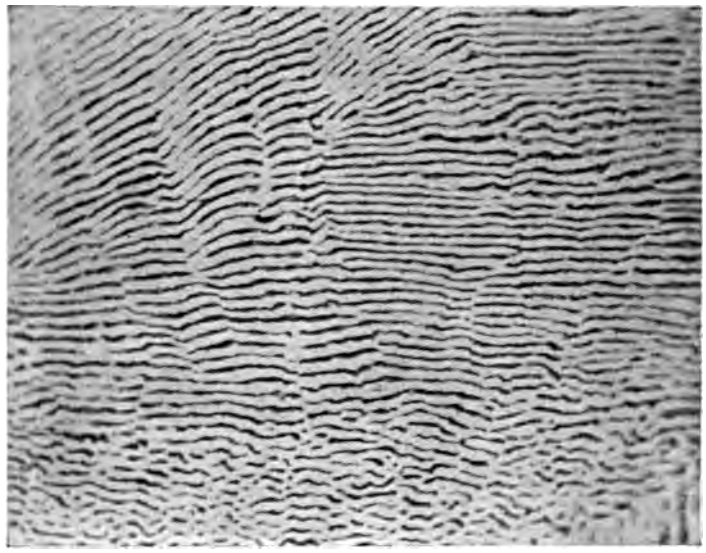

Fig. 19. — Eutectic (eutectoid) alloy of iron and Fe_3C. Pearlite. Magnified 1000 diameters. (Law.)

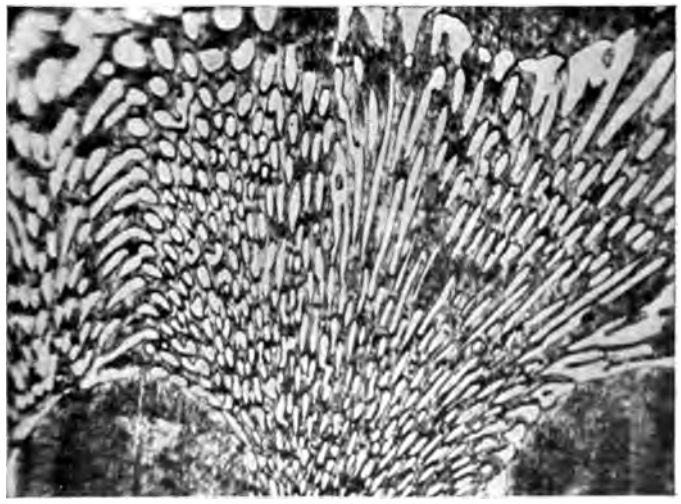

Fig. 20. — Eutectic alloy of $SnCu_4$ and Cu_3P. Magnified 1000 diameters. (Law.)

in the majority of cases being capable of retaining in solid solution a small percentage of the other metal. The modifications which such partial solubility introduces in the fusibility curve should be considered. Let us suppose two metals M and M' and let us assume that the metal M' is capable of retaining in solution immediately after

solidification, i.e. at the eutectic temperature, 5 per cent of the metal M and that the metal M can retain in solid solution 10 per cent of the metal M'. The fusibility curve of these alloys constructed in the usual way will have the appearance indicated in

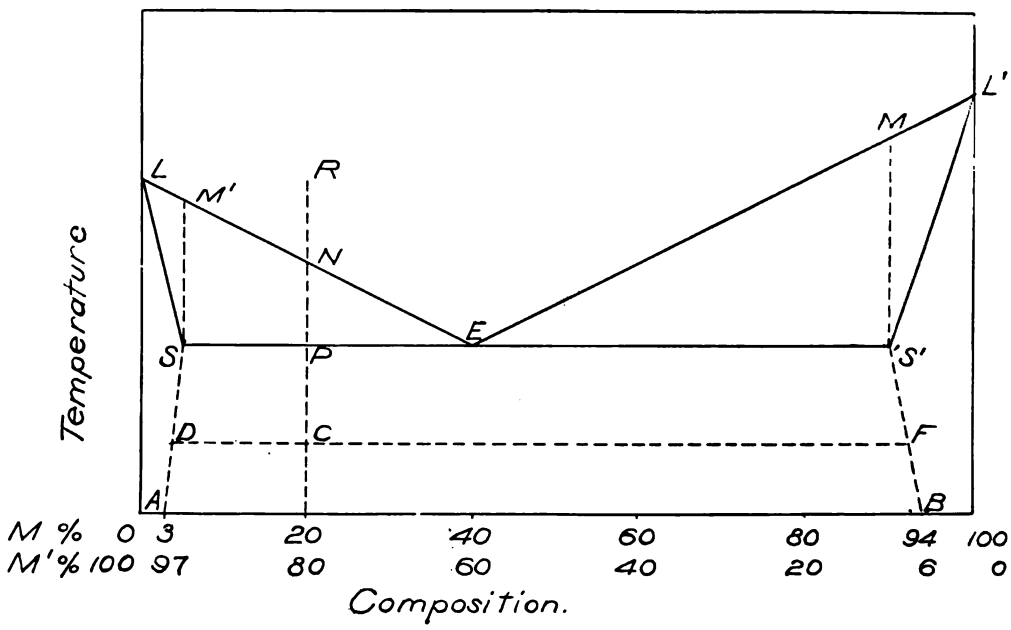

Fig. 21. — Typical fusibility curve of alloys whose component metals are partially soluble in each other in the solid state.

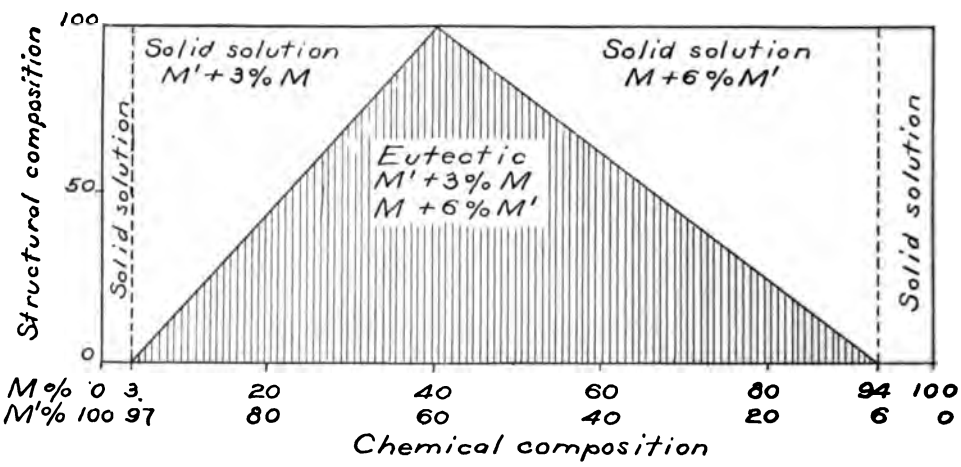

Fig. 22. — Diagram showing the structural composition of binary alloys whose component metal are partially soluble in each other in the solid state.

Figure 21. By comparing it with the fusibility curve of metals entirely insoluble (Fig. 12) it will be noted that the only differences between them are (1) that the eutectic line SES' instead of extending over the whole length of the diagram now stops at the points S and S' corresponding respectively to 5 per cent of metal M and to 10

per cent of metal M', and (2) the introduction of the branches SA and $S'B$ indicates the changes of solubility of the metals as the alloys cool from the eutectic to atmospheric temperature. These curves show that at atmospheric temperature M' retains in solution 3 per cent of M and that M retains in solution 6 per cent of M'. LEL' is the liquidus, $LSES'L'$ the solidus. Clearly, any alloy containing less than 5 per cent of the metal M or less than 10 per cent of the metal M' solidifies as a solid solution, the diagram showing the absence of eutectic alloys. In other words, alloys containing from 0 to 5 per cent of M may be considered as alloys of M' and of a solid solution of M' plus 5 per cent of M, LM' being the liquidus and LS the solidus of such alloys and their solidification taking place as explained in the case of any two metals forming solid solutions. And, likewise, alloys with less than 10 per cent of M' may be regarded as alloys of the metal M and of a solid solution of M plus 10 per cent of M', their liquidus being represented by $L'M$ and their solidus by $L'S'$. For all alloys containing between 5 and 90 per cent of M the diagram shows that a eutectic alloy is formed and that the mechanism of the solidification is apparently the same as the one

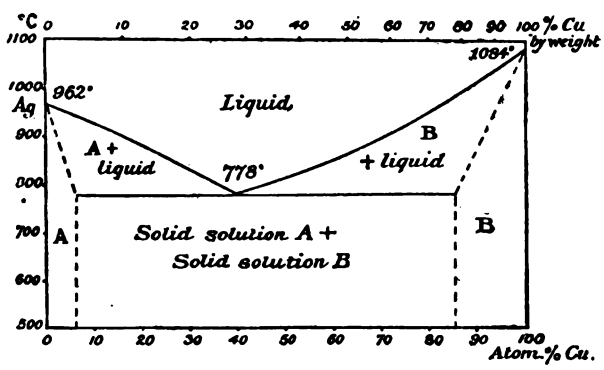

Fig. 23. — Fusibility curve of alloys of silver and copper. (Desch.)

described in the case of alloys of insoluble metals. It should be noted, however, that the two components of these alloys are no longer the pure metals but two solid solutions, namely, a solution of M' containing 5 per cent of M and a solution of M containing 10 per cent of M', one of these solid solutions, therefore, crystallizing when the temperature of the alloy reaches any point on the lines LEL' and the eutectic alloy being made up of a fine conglomerate of these two solid solutions. To clarify let us consider an alloy represented by the point R, Figure 21. At N its solidification begins, crystals of a solid solution of M' containing 5 per cent of M being formed. At P the residual molten mass, having reached the eutectic ratio, crystallizes at a constant temperature as a fine aggregate of the two solid solutions. Since the mutual solubilities of the metals M and M' decrease, however, as the alloy cools below the eutectic temperature, it is evident that each crystal must undergo a gradual transformation. These transformations are indicated by the branches SA and $S'B$. After the solidification of the eutectic, all alloys are aggregates of the two solid solutions whose compositions are represented by the points S and S', that is, in the case under consideration, arbitrarily, M' plus 5 per cent of M and M plus 10 per cent of M'. At atmospheric temperature all alloys are aggregates of two solid solutions whose compositions correspond to the points A and B, that is in the case considered M' plus

and M plus 6 per cent of M'. At any point below the eutectic line, the corresponding alloy is an aggregate of two solid solutions whose compositions are indicated by the corresponding points on the branches SA and $S'B$. At C, for instance, in case of alloy R, the structure is composed of free crystals of solid solution D and of eutectic, the components of which are solid solution D and solid solution F. In other words, as the alloy cools from the eutectic line to atmospheric temperature, the composition of its two constituents shifts respectively from S to A and from S' to B.

Fig. 24. — Silver-copper alloy. Copper 15 per cent. Magnified 600 diameters. Dark constituent is silver containing a little copper. (Osmond.)

Fig. 25. — Silver-copper alloy eutectic. Copper 28 per cent. Magnified 600 diameters. (Osmond.)

Fig. 26. — Silver-copper alloy. Copper 65 per cent. Magnified 600 diameters. Light constituent is copper containing a little silver. (Osmond.)

The structural composition of alloys whose component metals are partially soluble when solid may be represented in the usual way as shown in Figure 22. Its interpre-

tation does not call for further elaboration. Between 0 and 3 per cent of M and between 0 and 6 per cent of M', solid solutions are formed of corresponding compositions. Between 3 and 40 per cent of M, the free solid solution formed is saturated with M, and between 40 and 94 per cent of M it is saturated with M', while the eutectic is made up of the two saturated solutions. The fusibility curve of silver-copper alloys is shown in Figure 23 as an example of alloys whose components remain partly soluble in each other after solidification and typical structures of these alloys are given in Figures 24 to 26.

Examination

Describe briefly the mechanism of the solidification of binary alloys (1) completely soluble, (2) completely insoluble, and (3) partly soluble in each other in the solid state.

LESSON XXIII

EQUILIBRIUM DIAGRAM OF IRON-CARBON ALLOYS

Fusibility Curve of Iron-Carbon Alloys. — Steel and cast iron are essentially alloys of iron and carbon, and their fusibility curve or equilibrium diagram may be constructed as in the case of any binary alloy, namely, by determining the independent cooling curves of a number of alloys of the series and plotting the evolutions of heat

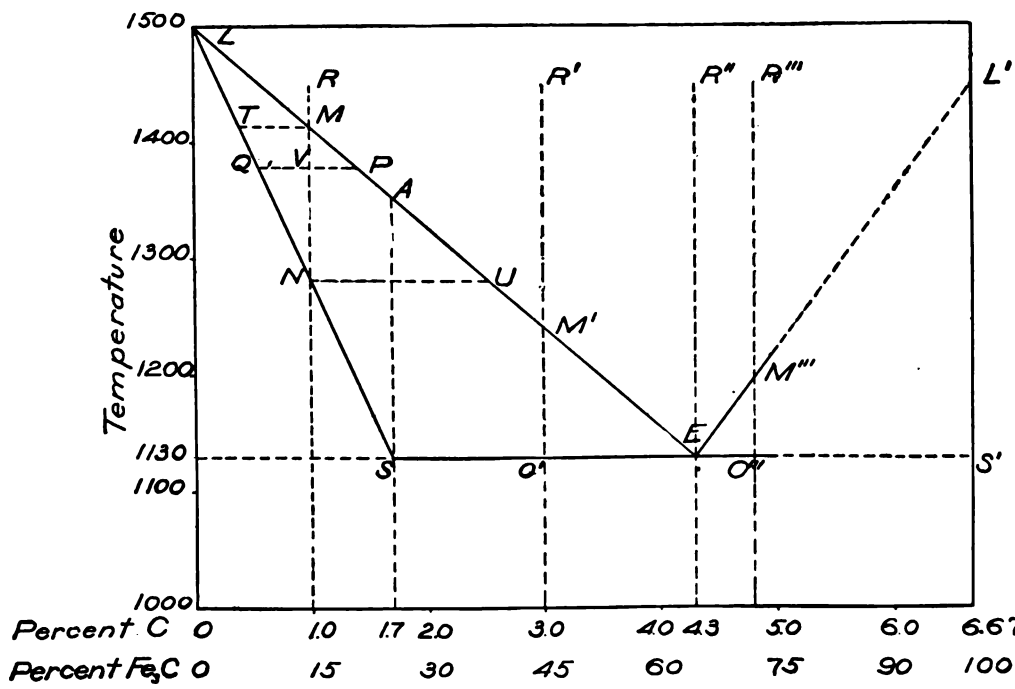

Fig. 1. — Fusibility curve of iron-carbon alloys.

noted against the corresponding temperatures. The resulting curve is shown in the diagram of Figure 1.

While it is not generally possible for molten iron to dissolve more than 5 per cent of carbon, the diagram has been constructed so as to include a percentage of carbon up to 6.67 per cent which corresponds to 100 per cent Fe_3C. That portion of it, however, corresponding to more than 5 per cent of carbon, has been drawn in dotted lines. The complete equilibrium diagram should include the evolutions of heat occurring after solidification, known as the critical points, which have been fully described in these lessons, but they are purposely left out of the diagram of Figure 1, it being desired first to confine our attention to the mechanism of the *solidification* of iron-

carbon alloys. In view of the explanation of the meaning of fusibility curves given in Lesson XXII, it will be evident that iron and carbon alloys are partially soluble in each other when solid, that *LEL'* is their liquidus and *LSS'* their solidus and that the point *E* indicates the formation of a eutectic alloy. As carbon increases from 0 to about 1.70 per cent, the alloys solidify as solid solutions of corresponding carbon content, *LA* being the liquidus and *LS* the solidus. These solid solutions considered as microscopical constituents are called austenite. The solidification of alloys containing between 1.7 and 4.3 per cent carbon begins when their temperature reaches the line *LE*, crystals of a solid solution containing 1.70 per cent carbon (sometimes called saturated austenite), being then formed which keep on growing until the line *SS'*, temperature 1130 deg., is reached when, clearly, a eutectic is formed composed of

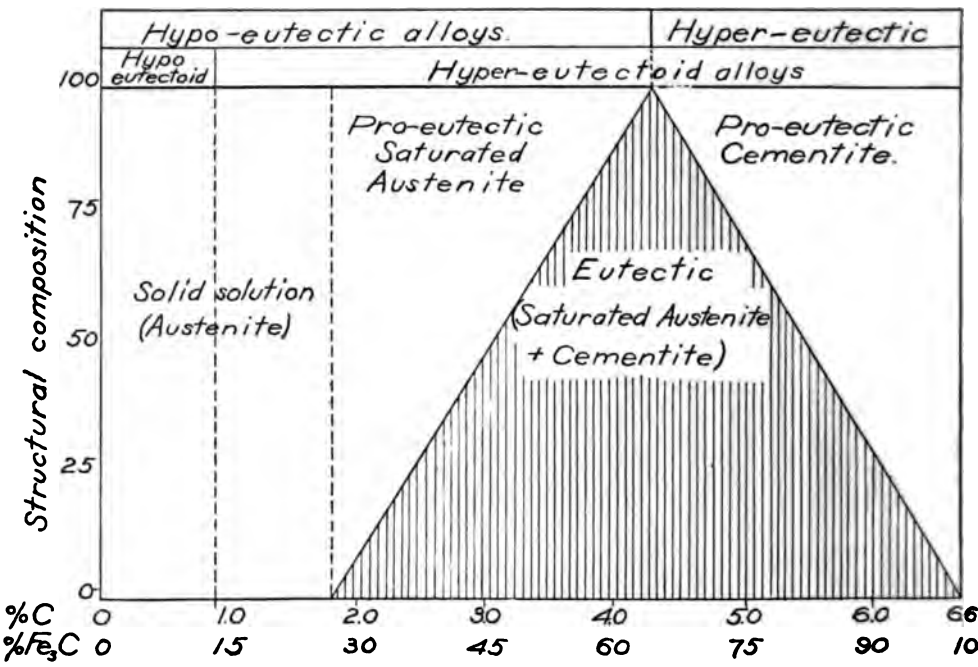

Fig. 2. — Structural composition of iron-carbon alloys immediately after their solidification.

that solid solution and of another constituent. The nature of the other constituent present in the eutectic alloy formed during the solidification of iron-carbon alloys has been in dispute. It seems at first natural to infer that elemental carbon, i.e. graphite, is that constituent, in which case the eutectic alloy would be made up of minute crystalline particles alternately of saturated austenite and of graphite. Many evidences, however, point to carbon being dissolved in molten iron as the carbide Fe_3C (cementite) and to its always solidifying as Fe_3C, although, as later explained, it may break up into iron and graphite ($Fe_3C = 3Fe + C$) immediately after its solidification. If this hypothesis be correct, it follows that the eutectic alloy must be a mechanical mixture of minute particles of saturated austenite and of Fe_3C. It would seem at first as if the microscopical examination of alloys of suitable compositions should readily reveal the nature of the eutectic alloy. It will soon be seen, however, that both cementite and graphite are generally found in solidified eutectiferous alloys, the microscopical test leaving us in doubt as to which of the two constituents formed first. In the

author's opinion it seems more probable that when an iron-carbon alloy containing more than some 1.7 per cent carbon solidifies, a eutectic of saturated austenite and of cementite is always produced, or in other words, that in the diagram of Figure 1 the curve $L'E$ indicates the crystallization of cementite and not of graphite. The opposite view will be considered later. Let us now follow the solidification of four typical alloys, namely, R, R', R'', R''', containing respectively 1 per cent, 3 per cent, 4.3 per cent, and 4.8 per cent of carbon, the first two being, therefore, hypo-eutectic alloys, the third the eutectic alloy, and the fourth a hyper-eutectic alloy. As the alloy R cools, it begins to solidify at M through the formation of crystals of a solid solution the composition of which is represented by the point T on the solidus. On cooling from M to N these crystals grow through successive additions of crystalline matter, the composition of which varies from T to N while the composition of the molten bath shifts from M to U, the last drop solidifying having the composition U. As soon as the crystalline matter is deposited, however, at least if time be given, diffusion takes place through each crystal so that finally they are chemically homogeneous and of composition N, the completely solidified metal being composed of homogeneous crystalline grains of austenite containing one per cent carbon.

At any temperature V between the solidus and the liquidus the crystals in equilibrium with the molten metal must have the composition Q. It may at least be conceived that if the cooling through and below the solidification period be rapid, the crystalline grains of austenite will not be chemically homogeneous, complete diffusion having been prevented.

In the case of an alloy whose composition is represented by the point R' in the diagram, it begins to solidify at M' (some 1230 degrees C.), when crystals of iron containing 1.70 per cent of carbon (saturated austenite) begin to form, the composition of the molten metal meanwhile shifting from M' to E. At O', temperature 1130, the residual molten mass has reached the eutectic composition and now solidifies at a constant temperature, namely, the eutectic temperature, the completely solid metal being made up of crystalline grains of saturated austenite surrounded by a eutectic alloy composed of minute crystals of saturated austenite and minute crystals of cementite.

The alloy R'' has the eutectic composition (4.3 per cent carbon). It remains liquid until its temperature falls to 1130 deg. C. when it solidifies at a constant temperature after the fashion of eutectic alloys.

The alloy R''' contains more carbon than the eutectic alloy. On reaching its solidification point M''' crystals of cementite begin to form, increasing in size as the metal cools from M''' to O''' while the composition of the bath shifts from M''' to E. At O''' the residual molten mass having now the composition of the eutectic alloy, freezes at a constant temperature, the completely solidified alloy being made up of crystals of cementite embedded in a ground mass consisting of the eutectic alloy.

Structural Composition of Iron-Carbon Alloys Immediately after Solidification. — The structural composition of iron-carbon alloys *immediately after their solidification*, assuming that Fe_3C and not graphite forms, may be represented in the usual way by the diagram of Figure 2. The diagram clearly shows (1) that alloys containing less than 1.70 per cent of carbon are made up wholly of solid solutions, (2) that alloys containing between 1.70 and 4.3 per cent carbon are made up of decreasing proportions of saturated austenite and increasing proportions of eutectic, (3) that alloys containing exactly 4.3 per cent of carbon are composed entirely of eutectic, and (4) that alloys containing more than 4.3 per cent carbon contain an increasing amount of free

cementite, and decreasing amount of eutectic the latter disappearing altogether when the metal contains 6.67 per cent carbon.

A modified form of the structural composition diagram may profitably be combined

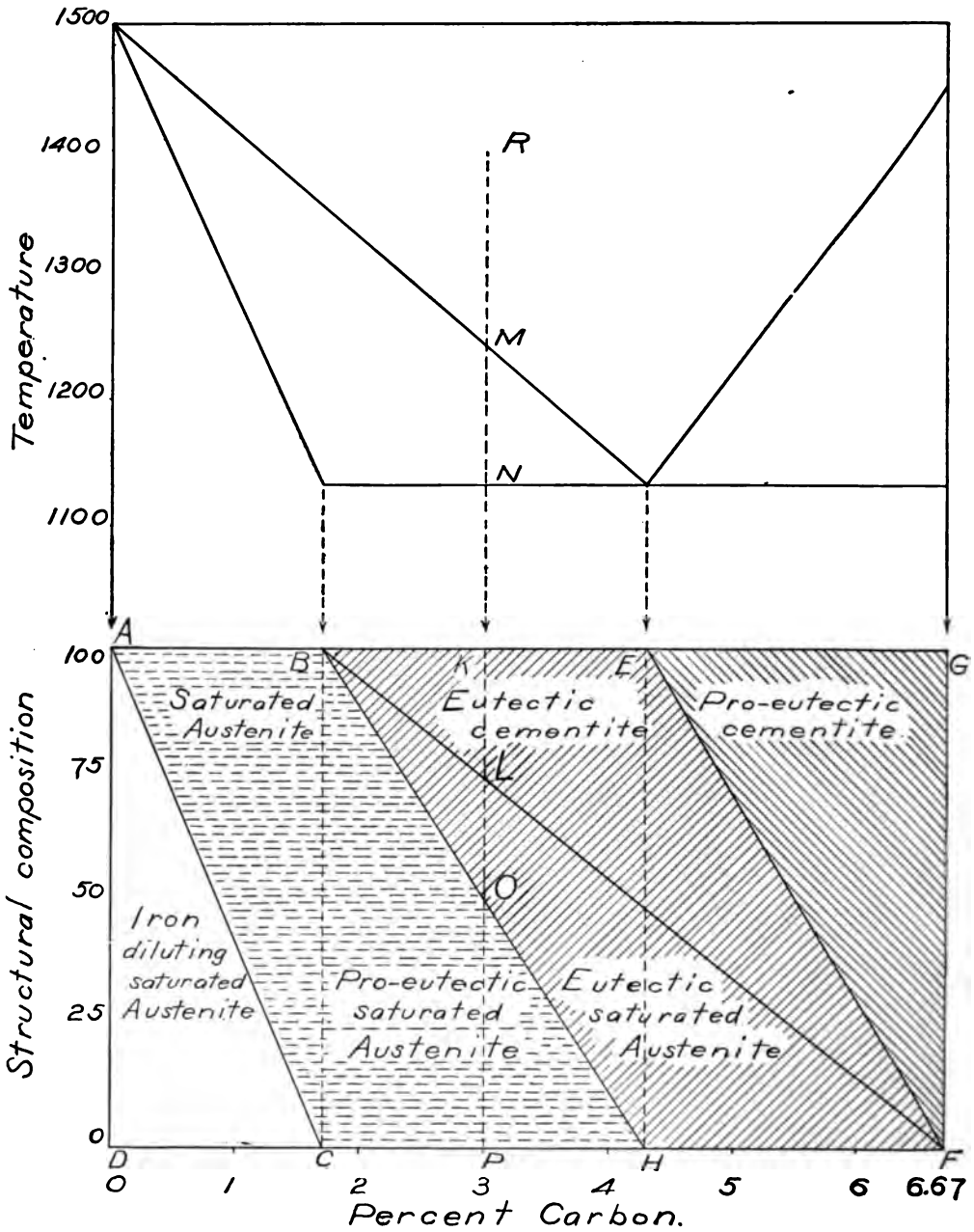

Fig. 3. — Fusibility curve and structural composition diagram of iron-carbon alloys.

with the equilibrium diagram as shown in Figure 3. Its interpretation should be obvious. The area *ABCD* represents the structural composition of all alloys containing less than 1.7 per cent of carbon, and shows that they are made up of 100 per cent

of austenite. By dividing this area by the line *AC*, however, it is further shown graphically that the composition of the austenite of these alloys varies, and that they may be considered as being made up of *ABC* saturated austenite *diluted* by *ADC* pure iron, clearly indicating that with 0 carbon the alloy is entirely made up of iron and with 1.7 per cent carbon entirely of saturated austenite. The area *BCH* represents the proportion of free (pro-eutectic) saturated austenite formed during the solidification of any alloy containing between 1.70 and 4.3 per cent carbon. The area *BEFH* represents the proportion of eutectic present in any alloy containing more than 1.7 per cent of carbon. By dividing this area in two portions, moreover, by means of the line *BF* we show graphically the relative proportions of saturated austenite and of cementite in the eutectic. Finally, the area *EGF* indicates the percentage of pro-eutectic

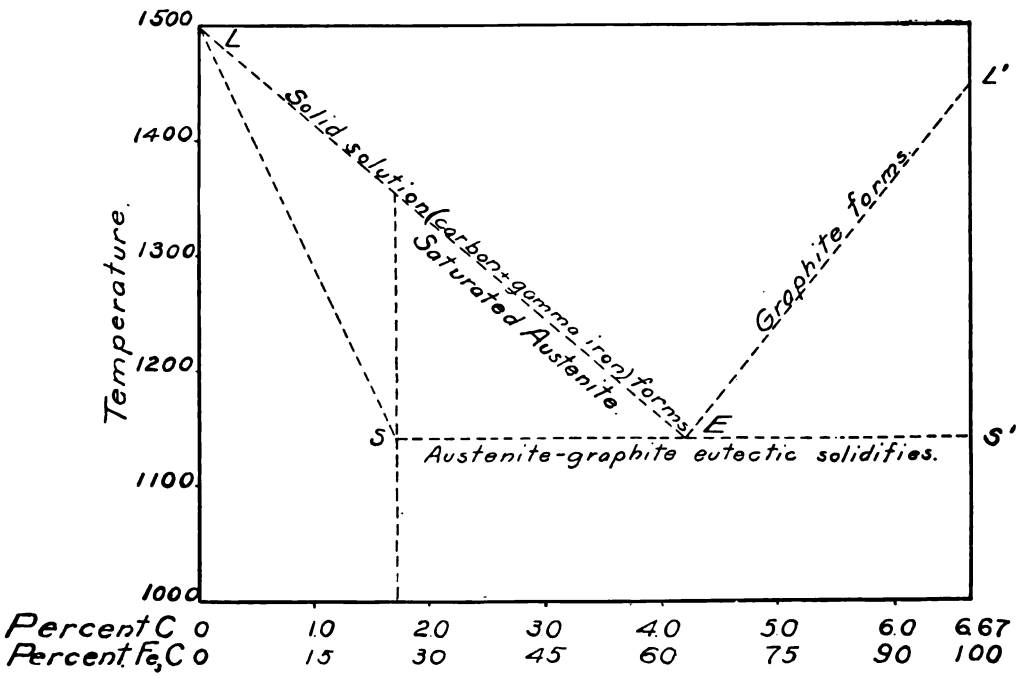

Fig. 4. — Iron-graphite fusibility curve of iron-carbon alloys.

cementite in any alloy containing more than 4.3 per cent carbon. To clarify, let us consider the alloy of composition *R* (3 per cent carbon). As it cools from *M* to *N* an amount of saturated austenite crystallizes, represented in percentage by the line *OP* of the structural composition diagram. At *N* an amount of eutectic alloy is formed, represented by the distance *KO* made up of *KL* per cent of cementite and *LO* per cent of saturated austenite.

The percentage of cementite and of saturated austenite in the eutectic may be readily calculated by solving the equations

$$(1)\quad A + Cm = 100$$

$$(2)\quad \frac{1.7}{100} A + \frac{6.67}{100} Cm. = 4.30$$

in which A represents the percentage of austenite, and Cm the percentage of cementite in the eutectic alloy and which express the facts that the carbon present in the eutectic

tribution of graphitic carbon to be observed in the case of gray cast-iron castings. On the contrary, on the assumption that graphite results from the breaking up of cementite soon after its solidification, it is readily understood why, in spite of their very great difference in specific gravity, iron and graphite are found uniformly distributed in the various parts of castings. The microscopical examination of the structure of very slowly cooled castings does not reveal the existence of a graphite-austenite eutectic.

That cementite is unstable, being readily converted into iron and graphitic carbon, is also generally admitted. It is upon this instability of cementite that the important industrial operation of converting white cast-iron castings into graphitic malleable castings is based. And there is abundant evidence that the higher the temperature, the more readily is cementite dissociated, from which it follows that the higher the temperature at which cementite *forms* the more readily will it be converted into graphitic carbon. Bearing this in mind, and with the assistance of the diagram of Figure 3, let us look more closely into the graphitizing of cementite. The diagram shows clearly that, during the solidification of alloys containing more than 1.70 per cent of carbon, (1) some cementite forms as pro-eutectic cementite if the metal contains more than 4.3 per cent carbon, (2) some cementite forms as eutectic cementite in all alloys, (3) some cementite remains dissolved in the eutectic-austenite of all alloys, and (4) some cementite remains dissolved in the free austenite of alloys containing less than 4.3 per cent carbon. Considering first the free cementite, that is, the pro-eutectic and the eutectic cementite, it is evident that the former is formed at a higher temperature, and that the more carbon in the alloy the higher the temperature at which it begins to form. It seems safe to infer, therefore, that pro-eutectic cementite will break up into graphite and ferrite more readily than eutectic cementite, this being consistent with the well-known fact that hyper-eutectic alloys are generally rich in graphite even after relatively quick cooling. The presence of pro-eutectic cementite may also promote the formation of graphitic carbon because once this graphitizing process is started, it is likely to extend, if time be given, to the bulk of the cementite, first the eutectic cementite and later the austenite-cementite undergoing the change. Alloys containing less than 4.3 per cent carbon and consequently free from pro-eutectic cementite should not become graphitic as readily because of the lower temperature at which eutectic-cementite forms. If a large proportion of cementite be formed, however, that is, if the alloys contain more than 3 or 3.5 per cent of carbon, a certain amount of graphitizing is readily induced through slow cooling. With decreasing carbon the breaking up of cementite becomes progressively more difficult until, in alloys containing less than 1.7 per cent carbon (the steel series), and, therefore free from eutectic cementite, graphitic carbon is very seldom formed.

It should be borne in mind that while those alloys which contain but a small proportion of carbon cannot be made graphitic, when a large proportion of carbon is present, the graphitizing once started may be made to include the totality of the cementite, thus explaining the freedom of steel from graphite and the freedom of some cast irons from cementite.

The foregoing remarks apply to pure iron-carbon alloys, the influence of the elements generally present in commercial products having been purposely ignored. When dealing with commercial steel and cast iron, the well-known influence of silicon in promoting the formation of graphitic carbon should be remembered as well as the opposite influence of sulphur and manganese. Because of the presence of a notable

Fig. 6. — Magnified 50 diameters.

Fig. 7. — Magnified 750 diameters.

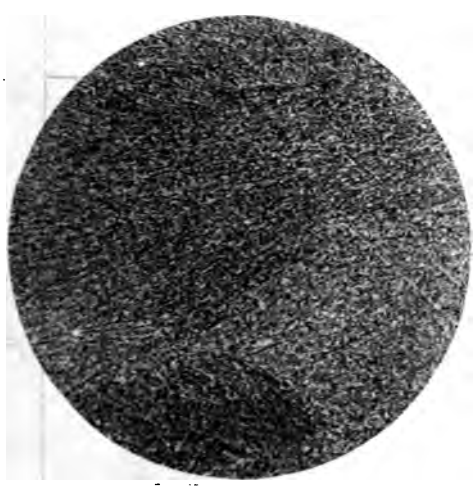

Fig. 8. — Magnified 50 diameters.

Fig. 9. — Magnified 750 diameters.

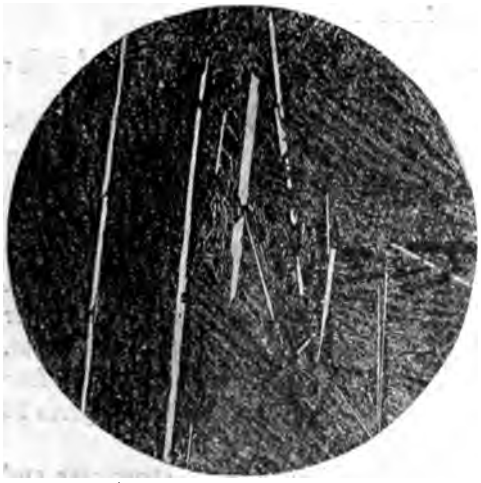

Fig. 10. — Magnified 50 diameters.

Fig. 11. — Magnified 750 diameters.

Figs. 6 and 7. — Iron-carbon alloy. Hypo-eutectic. Structure immediately after solidification. Dark crystallites of **saturated austenite** in a matrix of austenite-cementite eutectic. Figs. 8 and 9. — Iron-carbon alloy. Austenite-**cementite eutectic.** Figs. 10 and 11. — Iron-carbon alloy. Hyper-eutectic. Structure immediately after solidification. **Needles** of cementite in a matrix of austenite-cementite eutectic. (Gœrens.)

proportion of silicon, commercial cast irons after slow cooling are necessarily more graphitic than pure alloys of same carbon content.

Structure of Iron-Carbon Alloys Immediately after Solidification. — If the alloy contains less than some 1.70 per cent carbon it is made up after complete solidification of crystalline grains of austenite. It has been explained, however, that in the absence of manganese or other "retarding" elements it is not possible to prevent, even through very rapid cooling, the transformation of some of the austenite at least into martensite. The polyhedric structure of austenite has been illustrated in these lessons in the case of special steels (manganese and nickel steels) and it is now well understood that the

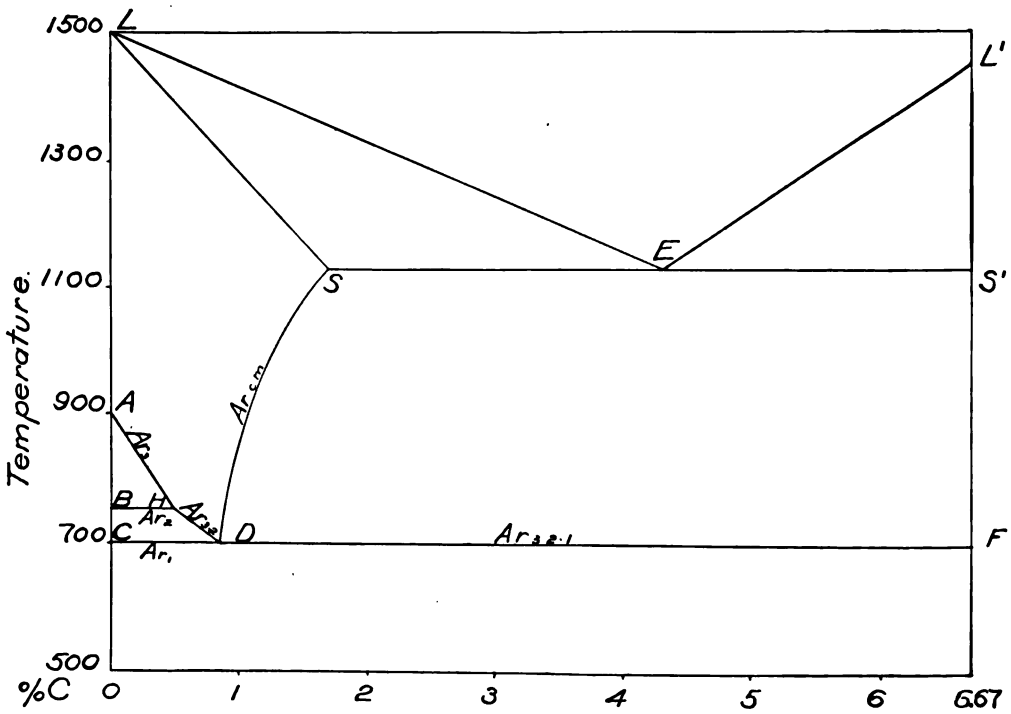

Fig. 12. — Equilibrium diagram of iron-carbon alloys.

frequent network structures of slowly cooled steel are due to the existence of polyhedric austenitic structures above their critical range.

If the alloy contains from 1.70 to 4.3 per cent carbon it is made up, after solidification, of crystals of saturated austenite and of eutectic alloy. This is well shown after Gœrens in Figure 6, in which the dark "pine tree" crystals consist of saturated austenite, while the ground mass is the cementite-austenite eutectic. In Figure 7 the same structure is shown more highly magnified. If the alloy contains exactly 4.3 per cent carbon, it consists wholly of eutectic as shown under different magnifications in Figures 8 and 9. It has been seen that, theoretically, this eutectic contains 47.7 per cent of saturated austenite (the dark constituent), and 52.3 per cent of cementite. Alloys containing more than 4.3 per cent carbon consist after solidification of free cementite in the form of needles embedded in a eutectic matrix as shown in Figures 10 and 11.

It should be noted that the dark constituent occurring in these structures and described as saturated austenite may not be absolutely unaltered austenite because of

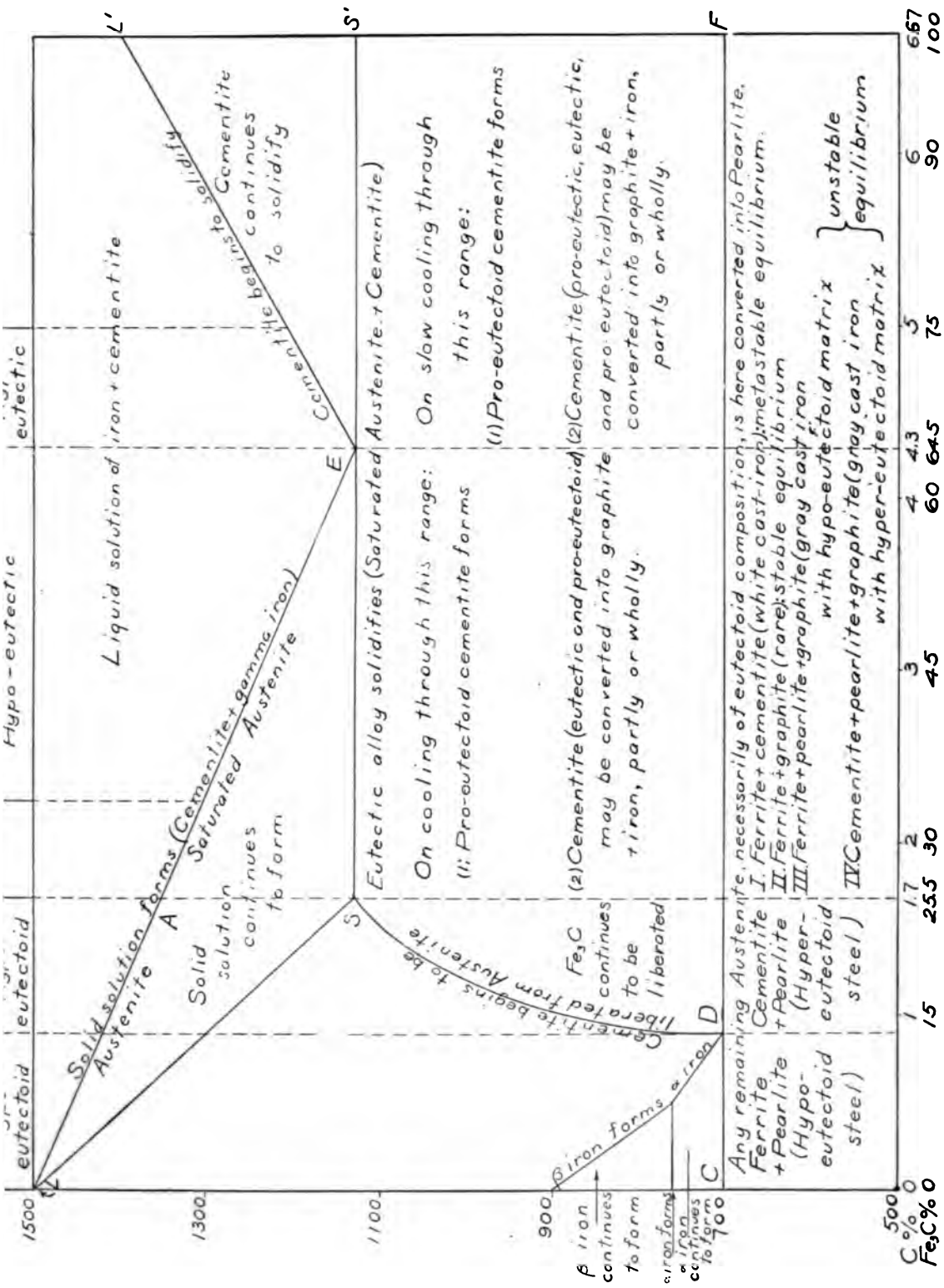

Fig. 13. — Equilibrium diagram of iron-carbon alloys with description.

the difficulty of completely preventing the transformation of that constituent even in the presence of a large amount of carbon and by very sudden cooling. If the austenite has undergone some transformation, however, so that it contains some martensite and even troostite those transformations must have taken place *in situ* and the structures reproduced in Figures 6 to 11 must represent accurately the structural aspect of the corresponding alloys after solidification.

Complete Equilibrium Diagram. — In the foregoing pages only the solidification curves of iron-carbon alloys have been considered and the probable mechanism of their freezing explained. Their equilibrium diagram, however, must include all heat evolutions observed on cooling from the liquid condition to atmospheric temperature; in other words, the thermal critical points fully described in previous lessons are part of the complete equilibrium diagram as indicated in Figure 12.

Since the meaning of every curve of this diagram has been discussed, it only remains to inquire into any possible structural or other changes taking place *after* solidification and *before* the alloys reach their respective thermal critical point or points, that is, while they cool from the solidus *LSS'* to the eutectoid line *CDF*. The changes which do or may take place as the alloys cool in this range are clearly stated in Figure 13. In this diagram the most likely significance of every curve is indicated as well as the nature of all structural transformations, and of all possible resulting structures after complete cooling. The author believes that it embodies those inferences best supported by analogy and by experimental evidences. Although necessarily involving some repetition, a methodical examination of the various parts of this complete diagram seems advisable, as it will permit a recapitulation of the various matters previously discussed.

Let us consider (1) the solidification of iron-carbon alloys, (2) their cooling from the solidus *LSES'* to the eutectoid temperature *CDF*, and (3) their cooling through the eutectoid temperature and their final structures.

According to the mechanism of their solidification iron-carbon alloys are divided into three classes, namely, (1) alloys containing less than 1.70 per cent of carbon, (2) alloys containing between 1.70 and 4.3 per cent carbon, and (3) alloys containing more than 4.3 per cent of carbon. Alloys containing less than 1.70 per cent of carbon and including, therefore, all the steels of commerce solidify as solid solutions of the carbide Fe_3C (cementite) in gamma iron, these solutions being known as austenite. *LA* is the liquidus and *LS* the solidus of these alloys. Alloys containing between 1.70 and 4.3 per cent of carbon solidify through the formation of crystals of saturated austenite at gradually decreasing temperatures and through the final solidification, at the eutectic temperature, of the residual molten metal necessarily of eutectic composition. Alloys containing more than 4.3 per cent of carbon solidify through the formation of cementite crystals at gradually decreasing temperatures, and through to final solidification, at the eutectic temperature, of the residual molten metal necessarily of eutectic composition.

In cooling below their solidus, *LS*, alloys with less than 1.70 per cent carbon undergo no change until they reach their thermal critical points Ar_3, $Ar_{3.2}$, $Ar_{3.2.1}$ or Ar_{cm} as the case may be, when, if they contain less than some 0.85 per cent of carbon (hypo-eutectoid steels), some iron is set free and converted into beta iron, while if they contain more carbon (hyper-eutectoid steels), cementite is liberated. In either case when the eutectoid temperature is reached the residual austenite, now of eutectoid composition (0.85 per cent carbon), is converted into pearlite.

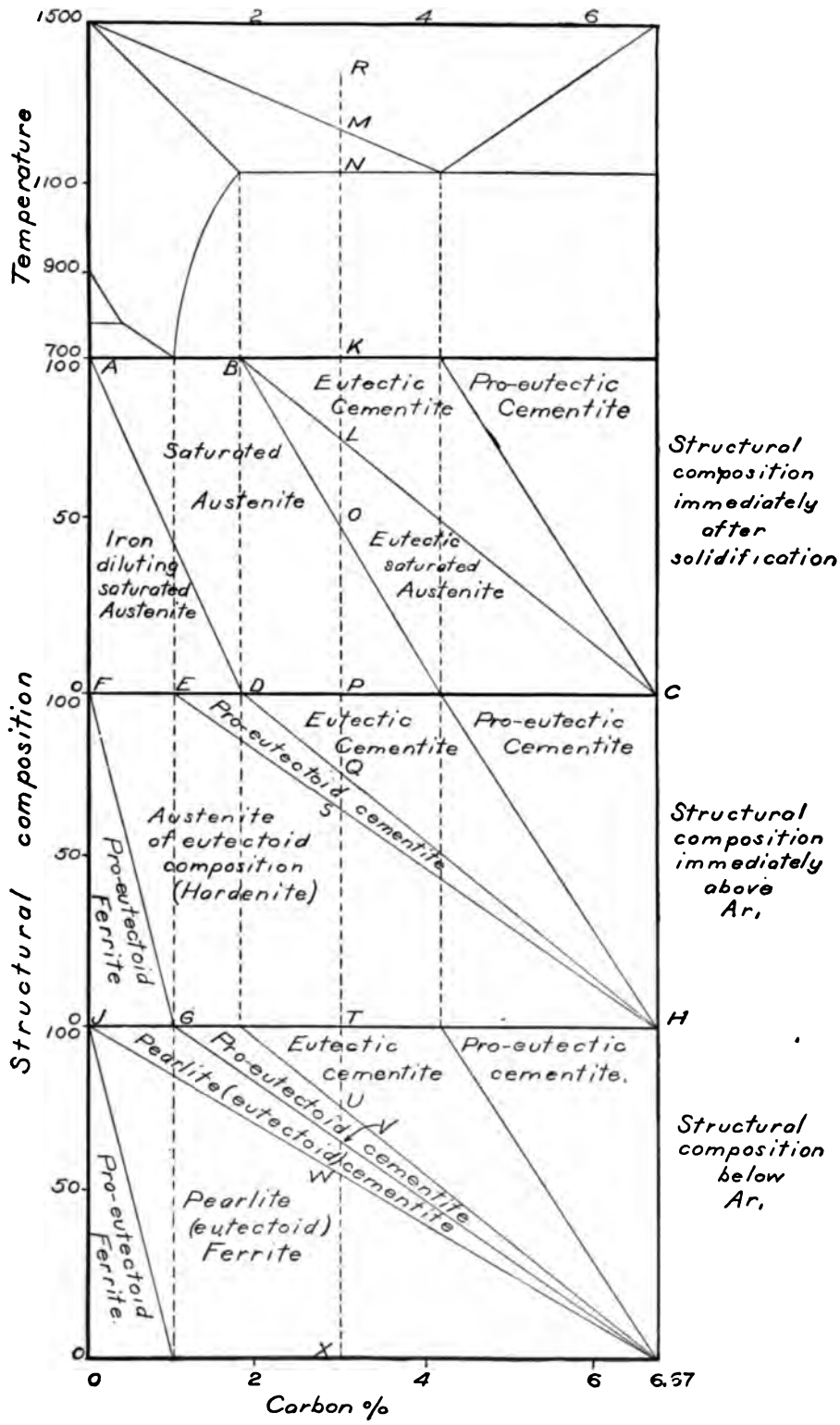

Fig. 14. — Equilibrium and structural composition diagram of iron-carbon alloys.

After solidification, alloys containing between 1.70 and 4.3 per cent carbon are aggregates of saturated austenite (austenite containing 1.70 per cent C or 25.5 per cent cementite) and of cementite-austenite eutectic. On cooling below their solidus, cementite (pro-eutectoid cementite) is liberated both from the free and from the eutectic-austenite, while if the cooling be sufficiently slow both the eutectic and pro-eutectoid cementite may be partly or wholly dissociated into graphite and iron (ferrite). Indeed, the graphitizing may even include the eutectoid cementite, in which case the alloy is made up solely of ferrite and graphite.

Alloys containing more than 4.3 per cent of carbon are, immediately after solidification, aggregates of cementite (pro-eutectic cementite) and of cementite-austenite eutectic. On slow cooling below their solidus, cementite (pro-eutectoid cementite) is liberated from the eutectic austenite while the pro-eutectic, eutectic, and pro-eutectoid

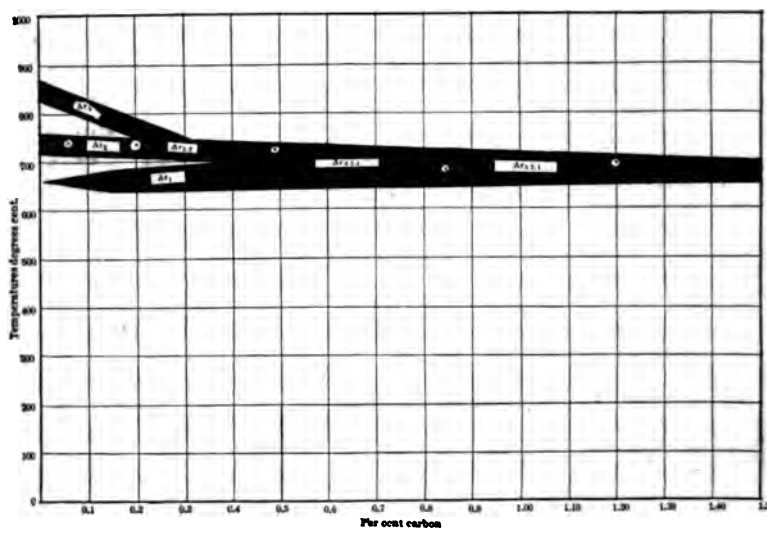

Fig. 15. — The author's early equilibrium diagram (1896).

cementite may be partly or wholly dissociated into graphite and ferrite, in some extreme cases the eutectoid cementite even being graphitized.

On cooling through the eutectoid temperature, any remaining austenite is bodily converted into pearlite.

The above consideration clearly shows that in alloys containing more than some 1.70 per cent carbon four types of structure may be formed according to the rate of cooling below the solidus:

(I) Cementite plus pearlite, the structure of white cast iron, readily produced by quick cooling and representing a metastable equilibrium. (II) Ferrite and graphite, an extreme case, possible only after very slow cooling and in the presence of much silicon, little manganese, and sulphur, and representing stable equilibrium. (III) Cementite plus pearlite and graphite, the structure of gray cast iron with hyper-eutectoid matrix, resulting from slow cooling, promoted by the presence of silicon and opposed by sulphur and manganese. (IV) Pearlite, ferrite, and graphite, the structure of gray cast iron with hypo-eutectoid matrix, produced because of slower cooling or because of the presence of more silicon or of less sulphur and manganese.

It will be explained in the next lesson that, according to the phase rule, only two components may be present in a binary alloy in a state of equilibrium from which it follows that gray cast irons, since they contain besides iron both cementite and graphite, are out of equilibrium. One of the components must disappear if the alloy is to assume equilibrium. Cementite is undoubtedly that component as proven by the malleablizing of cast iron when cementite is readily dissociated into graphite and ferrite on prolonged heating to a high temperature.

In Figure 14 the complete equilibrium diagram is shown combined with three constitutional diagrams showing graphically the structural composition of iron-carbon alloys (1) immediately after their solidification, (2) immediately before the eutectoid temperature, and (3) below the eutectoid temperature, *on the assumption that no graphitic carbon is formed.* The structural changes taking place while the alloys

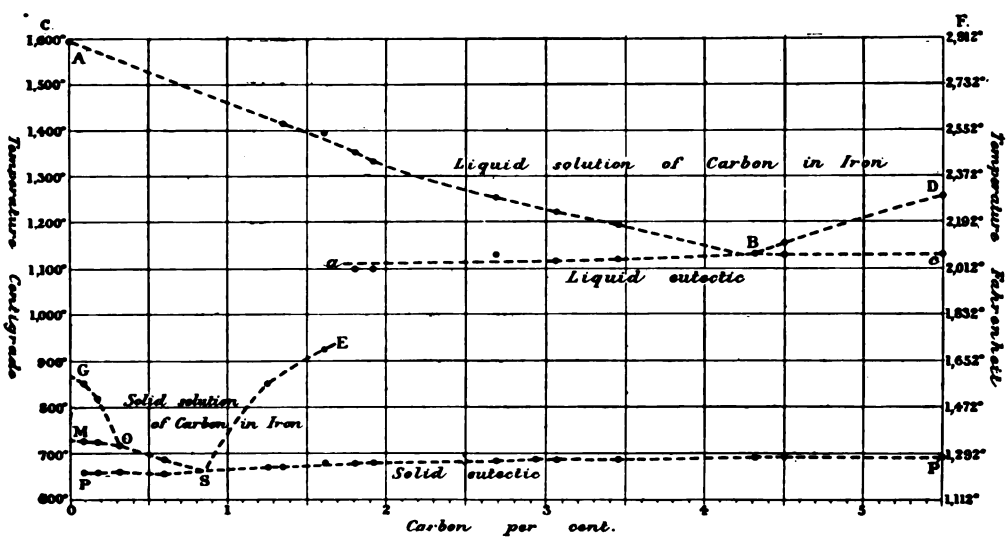

Fig. 16. — Roberts-Austen's first equilibrium diagram (1897).

cool below their solidus down to the eutectoid temperature are, in this way, clearly depicted. The following facts, for instance, are graphically shown, (1) the pro-eutectic cementite formed during the solidification of hyper-eutectic alloys and the eutectic cementite present in all alloys containing more than 1.70 per cent carbon remain unchanged as the alloy cools to atmospheric temperature, (2) the free saturated austenite of hypo-eutectic alloys, as well as the eutectic-austenite, are converted into eutectoid austenite through the liberation of cementite (pro-eutectoid cementite), the area *EDH* representing the cementite thus set free, and (3) in hypo-eutectoid alloys iron is set free as shown by the area *FJG*. The lower diagram shows that, in cooling through the eutectoid temperature, the remaining austenite, now necessarily of eutectoid composition, and sometimes called hardenite is converted into pearlite. Taking, for instance, the metal whose composition and temperature are represented by the point *R*, its transformations and final structure are clearly shown. At *M* it begins to solidify through the formation of crystals of saturated austenite; from *M* to *N* the austenite crystals continue to grow, the percentage of free austenite present in the solidified metal being represented by the distance *OP*; at *N* the residual bath

solidifies as a eutectic alloy, the percentage of which is proportional to the distance KO; this eutectic contains $KL = PQ = TU$ per cent of cementite and LO per cent of saturated austenite; LP is the total amount of austenite in the alloy; after solidification in cooling from N to K, pro-eutectoid cementite is liberated both from the free and from the eutectic-austenite, QS representing the percentage of cementite finally expelled; on reaching the point K, the remaining austenite, ST, is of eutectoid composition, when it is sometimes called hardenite, and in cooling through K this austenite is converted into pearlite, the metal being finally made up of TU per cent of eutectic cementite, UV per cent of pro-eutectoid cementite, and VX per cent of pearlite, the latter containing VW per cent of cementite, and WX per cent of ferrite, or of TV per cent of free cementite and VX per cent of pearlite, or again of TW per cent of total cementite and WX per cent of ferrite.

Historical. — In view of the scientific and practical importance of the equilibrium

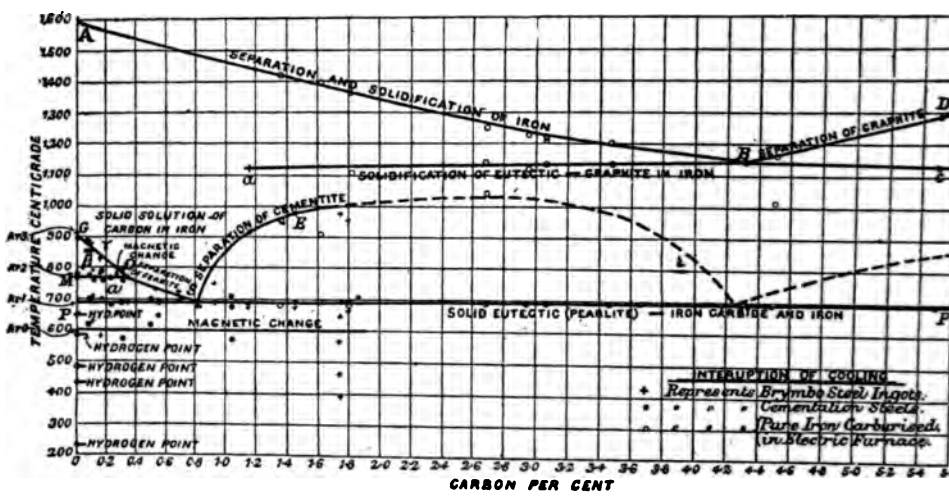
SEPARATION AND SOLIDIFICATION OF IRON
SEPARATION OF GRAPHITE
SOLIDIFICATION OF EUTECTIC — GRAPHITE IN IRON
SOLID SOLUTION OF CARBON IN IRON
SEPARATION OF CEMENTITE
MAGNETIC CHANGE
HYDROGEN POINT
SOLID EUTECTIC (PEARLITE) — IRON CARBIDE AND IRON
INTERRUPTION OF COOLING
Represents Brymbo Steel Ingots.
Cementation Steel.
Pure Iron Carburized in Electric Furnace.
TEMPERATURE CENTIGRADE
CARBON PER CENT

Fig. 17. — Roberts-Austen's second equilibrium diagram (1899).

diagram of iron-carbon alloys, a brief historical sketch of its evolution should be of interest to the reader. The first diagram was published by the author in 1896.[1] It is reproduced in Figure 15. It will be noted that, although the diagram includes only the thermal critical points, it is otherwise substantially accurate. In describing it the author wrote in part:

"Figure 1 shows graphically the position of the critical points in *cooling* steels of various carbons. The width of the black lines does not refer to the intensity of the retardations, but only indicates the range of temperature which they cover. For instance, it shows that the single retardation of high carbon steel begins at about 680 deg. C. and ends at about 640 deg. C. The maximum evolution of heat lies somewhere between these limits, but not necessarily in the middle.

" This graphical representation was obtained by plotting the results of the investigations of Osmond, Howe, Roberts-Austen, Arnold, and the writer; and, with one or two exceptions all their figures fall very nearly within the limits here indicated."

[1] "The Microstructure of Steel and the Current Theories of Hardening," ALBERT SAUVEUR, Transactions American Institute of Mining Engineers. 1896, p. 867.

It is from this modest beginning that the present diagram was evolved.

In 1897 Roberts-Austen published in his fourth report of the Alloys Research Committee of the Institution of Mechanical Engineers the diagram reproduced in Figure 16.

Two years later, in 1899, the diagram shown in Figure 17 was published by Roberts-Austen and Stansfield in the fifth report of the Alloys Research Committee. Some of the conspicuous features of this diagram should be noted. The solidification point of pure iron was indicated to be 1600 degrees C. whereas we know now that it is nearly 1500 deg. No attempt had been made yet at ascertaining the end of the solidification, that is, the solidus, of alloys forming solid solutions; the formation of a eutectic on solidification was indicated as taking place in alloys containing more than one per cent carbon; graphite was supposed to crystallize during the solidification of alloys con-

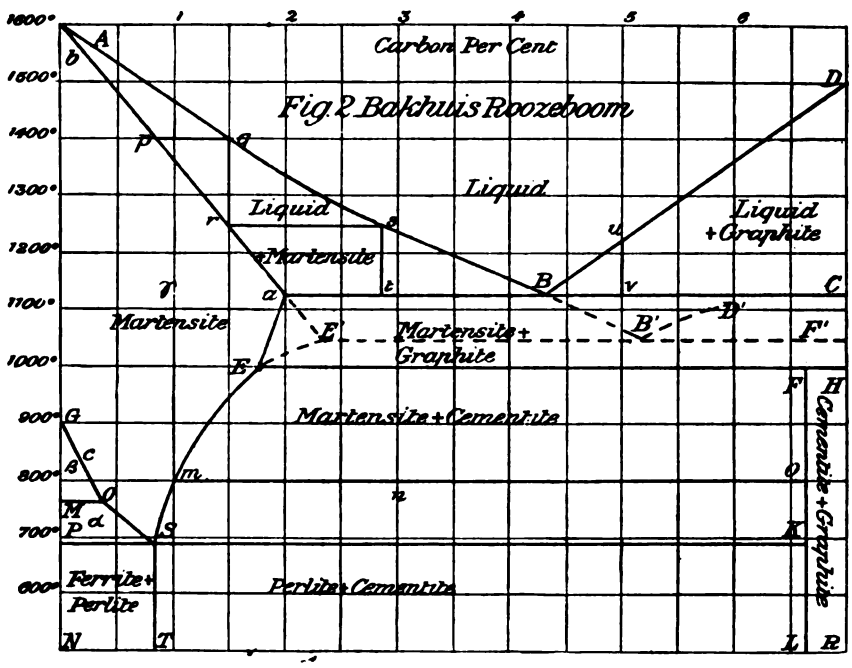

Fig. 18. — Roozeboom's equilibrium diagram (1900).

taining more than 4.3 per cent carbon, there being in the diagram no indications of possible formation of cementite; the eutectic alloy was assumed to be a graphite-iron eutectic; critical points occurring below the eutectoid temperature were represented in the diagram and marked "hydrogen points" (See Lesson VII, page 8, "Minor critical points"); the Ar_{cm} curve was arbitrarily extended to yield a V-shaped curve. Roberts-Austen mentioned the formation of a solid solution, free in hypo-eutectic steels, and as a constituent of the eutectic in alloys of eutectic composition, and he ascribed the presence of free cementite in cast iron to the liberation of that constituent from solid solution.

In 1900 Roozeboom took up the study of Roberts-Austen's diagram, and applying to it the teachings of the phase rule published the diagram of Figure 18 as a probably accurate representation of the solidification mechanism of iron-carbon alloys and of the structural transformations taking place after solidification. In this diagram, the line *ba*, that is, the solidus of alloys forming solid solutions, is for the first time indicated;

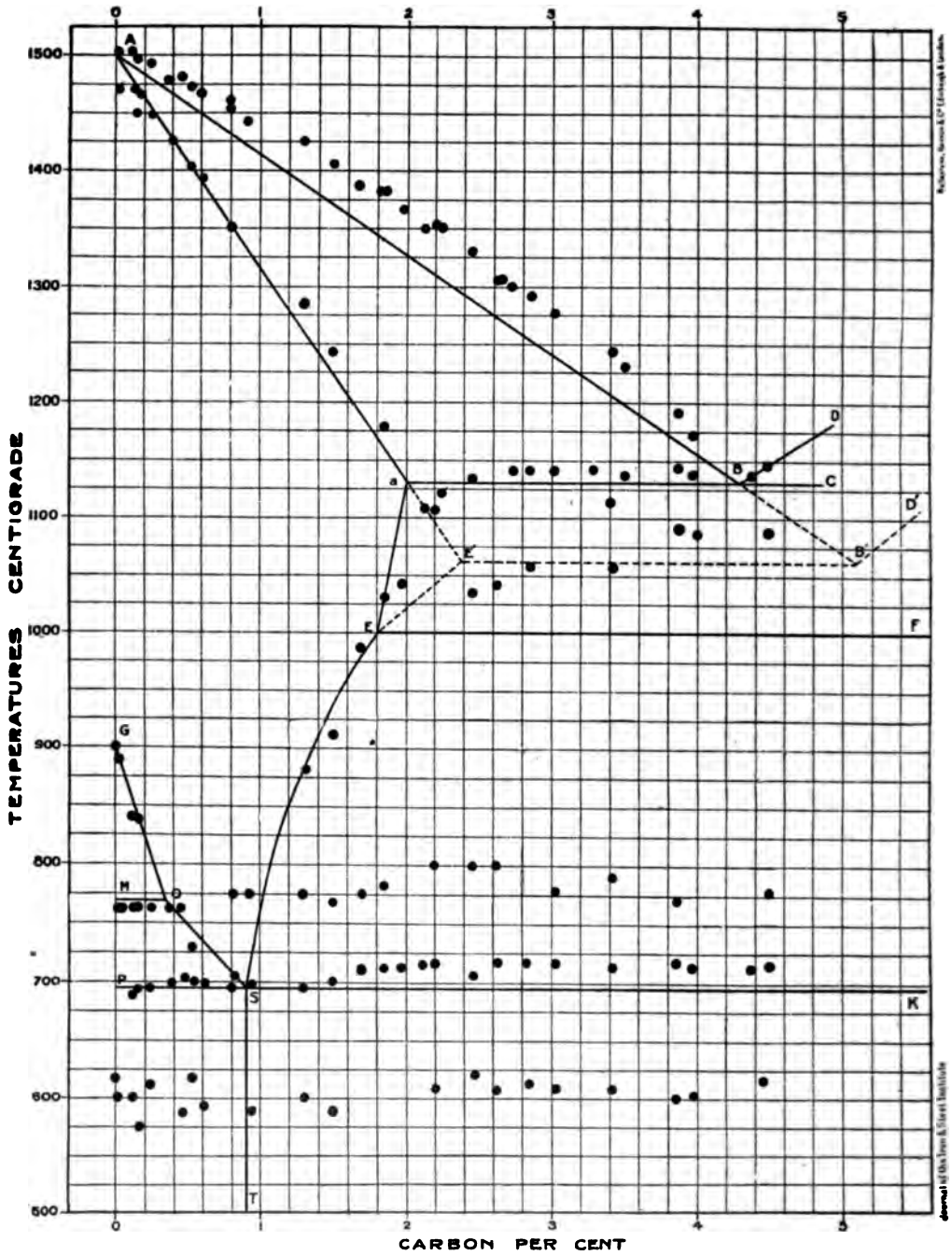

Fig. 19. — Carpenter's and Keeling's equilibrium diagram (1904).

the word martensite is used instead of austenite to denote the solid solution of iron and carbon; free graphite is assumed to form during the solidification of alloys containing more than 4.3 per cent carbon and the constituents of the eutectic alloy are supposed to be martensite (solid solution) and graphite. The Ar_{cm} curve of hypereutectoid steels is arbitrarily extended as an horizontal line starting from *E* (1.75 per cent carbon and 1000 deg. C.) and extending to the end of the diagram. Roozeboom argued that, while graphite formed on solidification in all alloys containing more than 2 per cent carbon, this graphite at 1000 deg. (line *EF*) recombined with iron to yield cementite so that, finally, alloys in equilibrium would contain only ferrite and cementite, thus conforming to the phase rule which forbids the presence of more than two components in binary alloys. It has since been conclusively shown that Roozeboom was in error, that while the ferrite-cementite system is in equilibrium according to the

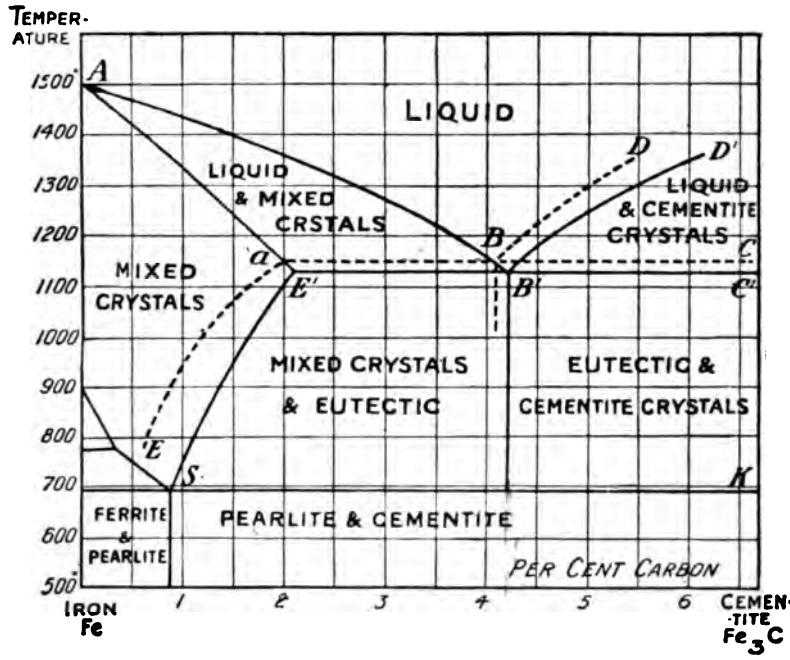

Fig. 20. — Benedicks' double equilibrium diagram.

phase rule, it is in metastable equilibrium, the ferrite-graphite system being the only stable one. The hypothetical horizontal line *EF* is now consequently omitted from the equilibrium diagram, and the Ar_{cm} curve made to join the eutectic line at its origin (*a*).

In 1904 Carpenter and Keeling made a series of very careful experiments in order to ascertain the evolutions of heat taking place in cooling pure iron-carbon alloys from the liquid state to atmospheric temperature. By plotting their results, the equilibrium diagram reproduced in Figure 19 was obtained. The solidification of pure iron is shown to take place at 1500 deg. C. The curves are otherwise identical to those of Roozeboom, the horizontal line *EF* having been introduced. The faint evolutions of heat occurring in the vicinity of 600 deg. C. already discovered by Roberts-Austen and ascribed by him to the presence of hydrogen, were also observed by Carpenter and Keeling, as well as some faint evolutions in the vicinity of 775 deg., the meaning of which remains uncertain.

When it became apparent that graphite and not cementite must be the final stable form of carbon, several authorities argued that two equilibrium conditions could exist according to the rate of cooling during solidification, one of them stable, the other metastable, and that this should be indicated in the diagram. This view was presented notably by Charpy and Grenet, by Benedicks and by Heyn. The double diagram advocated by them is represented in Figure 20. The solidification of free cementite and of the cementite-austenite eutectic being assumed to be due to the well-known phenomenon of surfusion or undercooling, the corresponding curves are arbitrarily outlined at temperatures slightly lower than those pertaining to the formation of free

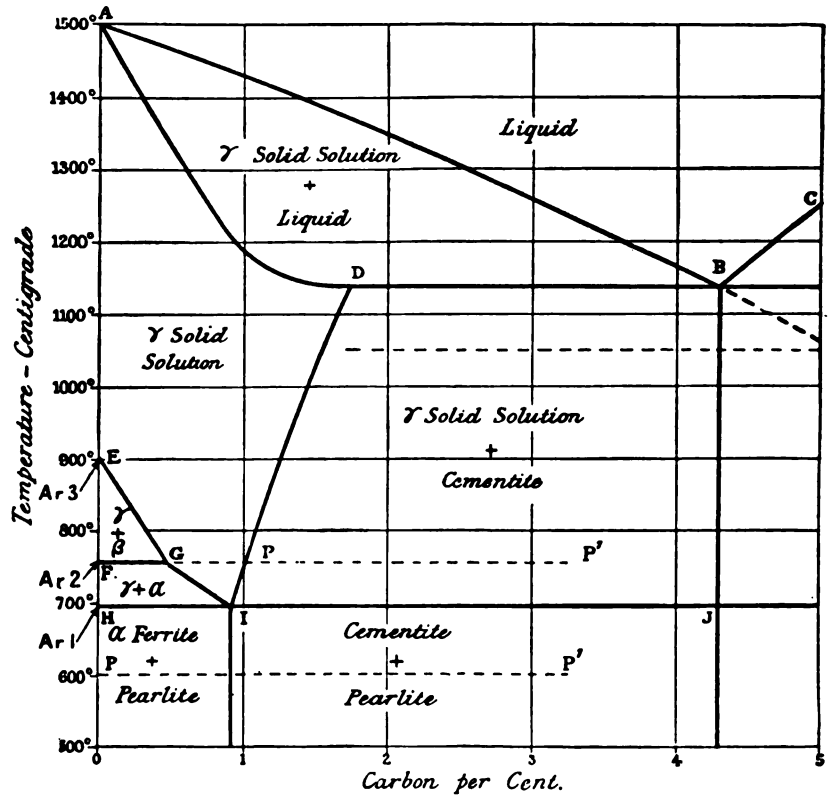

Fig. 21. — Rosenhain's equilibrium diagram (1911).

graphite and of graphite-austenite eutectic. The author has already shown why, in his opinion, the graphite curves should be left out. The view that cementite always forms during the solidification of iron-carbon alloys but that being unstable it is readily dissociated into ferrite and graphite, seems to be better supported by experimental evidences and more consistent with practical facts.

Rosenhain has recently plotted the experimental results of Carpenter and Keeling, of Gutowsky and of himself, obtaining the diagram reproduced in Figure 21. He considers Gutowsky's results in regard to the form of the solidus curve of alloys forming solid solutions as more accurate than those previously published, and he incorporates them in the diagram as shown in Figure 21, the solidus line being rounded instead of straight as heretofore represented. In justification of his course, Rosenhain writes:

"We have now to consider the curved portion of the 'solidus,' the line *AD*. This

represents the temperatures at which the alloys have just completed their freezing process, that is, have just become completely solid, or, conversely, it represents the temperature of incipient fusion on heating. In the earlier investigations, and even in those of Messrs. Carpenter and Keeling, these temperatures were obtained by estimating the point on each of the cooling-curves where the heat-evolution due to solidification came to an end. Unfortunately, the *end* of a heat-evolution is never sharply indicated on the curves, so that this estimation was admittedly vague. Quite recently that determination has been repeated, and with considerable greater accuracy, because a very much more satisfactory method was available . . .

"The method of determining the 'solidus' was to take small pieces of steel, of known composition, heat them, and suddenly cool them from successively higher temperatures; afterward each specimen was examined by means of the microscope.

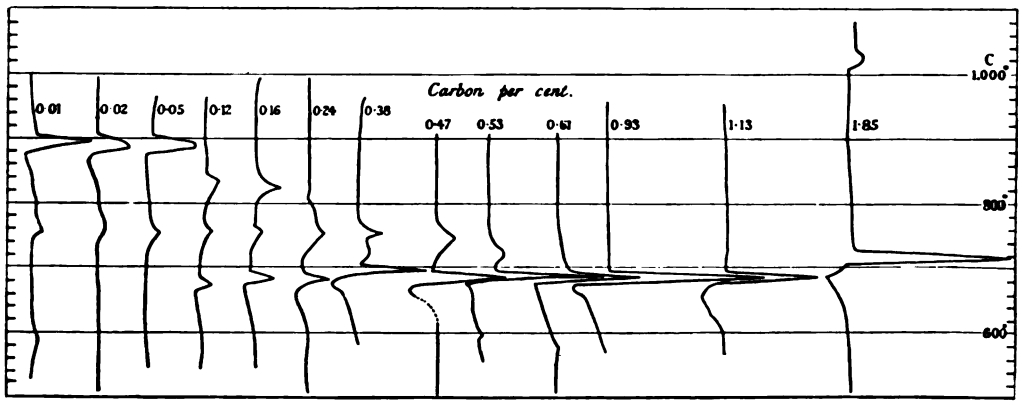

Fig. 22. — Cooling curves of carbon steels replotted from the data of Carpenter and Keeling. (Rosenhain.)

It is easy, as the photographs show, to determine what is the particular point at which you have reached a temperature where there was a small quantity of liquid metal present at the moment of quenching."

The data obtained by Carpenter and Keeling have been given in the form of a table in Lesson VII, page 9, and some of these curves reproduced in Figure 8, page 17 of the same lesson. Rosenhain has recently replotted some of the figures of Carpenter and Keeling by his derived differential method (Lesson VII, page 16) and obtained the sharp curves shown in Figure 22.

Examination

Describe briefly (1) the solidification, (2) the transformations after solidification and according to rate of cooling, and (3) the final structures of iron-carbon alloys containing respectively 1.25, 3.50, and 5.00 per cent carbon.

Calculate the structural composition of these alloys, assuming that graphitic carbon does not form, (1) immediately after solidification, and (2) below the eutectoid temperature.

LESSON XXIV

THE PHASE RULE

The Phase Rule to which references have been made in the preceding lessons should now be considered as it has been found of much assistance in interpreting correctly the iron-carbon equilibrium diagram.

Enunciation of the Phase Rule. — The phase rule was enunciated in 1878 by Willard Gibbs, at the time Professor of Physics in Yale University. It is one of the most notable contributions ever made to physical chemistry.

The phase rule deals with the *equilibrium* of systems and is generally expressed by the formula:

$$F = C + 2 - P$$

showing the relation existing between the *degrees of freedom* (F) of a *system*, the number of *components* (C), and the number of *phases* (P); it tells us that the number of degrees of freedom of any system is equal to the number of its components plus two, minus the number of phases present. In order to understand the phase rule and its application, it is necessary and sufficient to have an accurate understanding of the meaning of the terms employed in its enunciation, namely, equilibrium, degrees of freedom, components, and phases.

Equilibrium. — A substance or system may be said to be in a state of equilibrium when it is chemically and physically at rest, meaning by chemical rest that chemical compounds are neither being dissociated nor formed, and by physical rest, not the absence of motion but the absence of molecular transformation, such as changes of state or allotropic changes. It is necessary, however, to distinguish between *homogeneous* and *heterogeneous* substances. A substance is said to be homogeneous when it is chemically and physically uniform throughout, i.e. when any two portions of it possess identical chemical and physical properties. Homogeneous substances are necessarily gaseous mixtures, elements, chemical compounds, or liquid and solid solutions. The equilibrium of a homogeneous system is sometimes called homogeneous equilibrium. A heterogeneous substance is made up of two or more physically separate parts, that is, of parts having different physical properties. Ice and water, many rocks, and many alloys are instances of heterogeneous substances. If the component parts of heterogeneous substances may be present in indefinite proportions, the substances are mechanical mixtures; if they occur in definite proportions, the substances are eutectic or eutectoid alloys. The equilibrium of heterogeneous systems is sometimes called heterogeneous equilibrium.

Howe has recently suggested that the homogeneous constituents of alloys be called "metarals" because of the great analogy between the constitution of metallic alloys and of rocks, the minerals being the homogeneous components of the latter, while the word aggregate is very frequently used to designate heterogeneous alloys. In metal-

lography, therefore, metarals and aggregates may conveniently replace the equivalent terms, homogeneous and heterogeneous substances, of the physical chemist.

Only three independently variable factors can affect the equilibrium of a system, namely, (1) the temperature, (2) the pressure, and (3) the concentration or composition. If arbitrary values may be given to one or more of these factors without destroying the chemical and physical rest of the system, its equilibrium is said to be *stable.* On the contrary, if a change in value of any one of these three factors results in chemical or physical transformation, i.e. in atomic or molecular activity such as dissociation or formation of chemical compounds, changes of state, or allotropic changes, the equilibrium of the system was *unstable.* Water under atmospheric pressure is in stable equilibrium, for we may change its temperature within wide limits without causing it to undergo a change of state, while of course its chemical composition remains likewise unaffected. All elements are generally in a state of stable equilibrium, as well as an infinite number of substances composed of two or more elements, for they may be heated, for instance, through wide ranges of temperatures without upsetting their physico-chemical equilibrium. Examples of unstable equilibrium, however, are far from uncommon. During the solidification of substances, for instance, stages must generally be passed through during which the equilibrium of the substance is unstable, and it is often possible through very rapid cooling to retain in the cold the unstable conditions, because of the rigidity of the substance now opposing the changes needed for a return to stable equilibrium. It has been seen in these lessons that hardened steel is, for the above reason, unstable, hence the possibility of tempering it by slight reheating.

The kind of equilibrium known as *metastable* remains to be described. Liquids may be cooled, when taking the necessary precautions, below their normal freezing-point, without freezing, the phenomenon being known as superfusion, surfusion, or undercooling, and the substance being said to be in metastable equilibrium. Water, for instance, may be cooled below 0 deg. C. and still remain liquid. The introduction of a solid fragment of the substance, a piece of ice in the case of water, results in the solidification of the liquid while its temperature rises to its normal freezing-point. Otherwise, the substance may be kept liquid below its solidification point for any length of time. If the temperature of the liquid continues to fall, however, a point is reached when its equilibrium becomes *unstable,* i.e. when further lowering of temperature causes the liquid to solidify. To state the case broadly, the failure on the part of a system to undergo a certain chemical or physical transformation when that transformation is due, *although given the necessary time,* results in metastable equilibrium, while its failure to undergo a transformation *because of the necessary time being denied,* as in quenching, results in unstable equilibrium. Metastable equilibrium is stable, at least within narrow limits of temperature, while, theoretically at least, slight heating of a substance in unstable equilibrium should result in a partial return to a more stable condition, that is, in a partial occurrence of the transformation that was suppressed by quick cooling.

Degrees of Freedom. — By the degrees of freedom (sometimes called degrees of liberty), of a system is meant the number of the three independently variable factors, temperature, pressure, and concentration, which may arbitrarily be made to vary without disturbing the system's physico-chemical rest. It has already been noted that a system, in order to be in stable equilibrium, must have at least one degree of freedom. It will also be understood that no system can have more than two degrees of freedom because in the case of arbitrary values being given to two of the factors, the

value of the third is necessarily fixed, this being due to the known rigid relations existing between temperature, pressure, and concentration.

Systems which have no degree of freedom are said to be "unvariant" or "nonvariant." Their equilibrium is necessarily unstable. Systems having one degree of freedom are called "univariant" or "monovariant," and those with two degrees of freedom "bivariant" or "divariant."

Phases. — By the phases of a system are meant the *homogeneous*, physically distinguishable, and mechanically separable constituents of that system. Water and ice, for instance, are possible phases of the water-ice system; quartz, felspar, and mica are phases of quartz, that is, of the silica-alumina-potash system. It will be apparent that phases must necessarily be gaseous mixtures, elements, definite chemical compounds, or solutions. As previously mentioned, Howe, following the petrographical nomenclature, and noting that the minerals are the phases of rocks, calls "metarals" the phases of metals and alloys.

Components. — The components of a system are described by Findlay as "those constituents the concentration of which can undergo *independent* variation in the different phases," by Bancroft as "substances of independently variable concentration," by Mellor as those "entities which are undecomposable under the conditions of experiments," by Howe as "free elements and those compounds which in the nature of the case are undecomposable under the conditions contemplated, and so play the part of elements." The components of a system may be either chemical compounds or elements, but there is at times some difficulty in grasping the distinction between the components of a system and its ultimate chemical constituents. The criterion by which to decide whether an entity is or is not a component, is the possibility of independent variation in the different phases. Take the system water, for instance: evidently water and not hydrogen and oxygen is the component, because any variation in the proportion of hydrogen would necessarily imply a corresponding and well-defined variation in the proportion of oxygen and vice versa. Findlay writes:

"In deciding the number of components in any given system, not only must the constituents chosen be capable of independent variation, but a further restriction is imposed, and we obtain the following rule: *As the components of a system there are to be chosen the* **smallest number** *of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation.*"

In the case of alloys, however, such difficulty does not arise, for the constituent metals are always the components of the systems.

The Phase Rule Applied to Alloys. — In dealing with alloys we may for all practical purposes ignore the influence of pressure, seeing that because of their feeble volatility they are practically always subjected to atmospheric pressure. Omitting the influence of pressure necessarily reduces by one the possible number of degrees of freedom so that in the case of alloys the phase rule may be expressed by the formula:

$$F = C + 1 - P$$

signifying that the number of degrees of freedom is equal to the number of components plus one, minus the number of phases. Since to be in stable equilibrium a system must have at least one degree of freedom, it is obvious that an alloy made up of n metals cannot have more than n phases. If it had $n + 1$ phases it would have no degree of freedom, that is, its equilibrium would be unstable. With $n - 1$ phases it would have

two degrees of freedom. It could not have less than $n - 1$ phases, since it cannot have more than two degrees of freedom.

The Phase Rule Applied to Pure Metals. — Pure metals have only one component, but their possible phases are (1) liquid metal, (2) solid metal, (3) several allotropic conditions of the solid metal. Let us consider Figure 1, which represents the solidification of a pure metal as explained in Lesson XXII.

Above the temperature T the metal is entirely liquid; it has but one phase, and consequently one degree of freedom ($F = 1 + 1 - 1 = 1$). The system above T is univariant; its temperature may be altered within wide limits without disturbing its

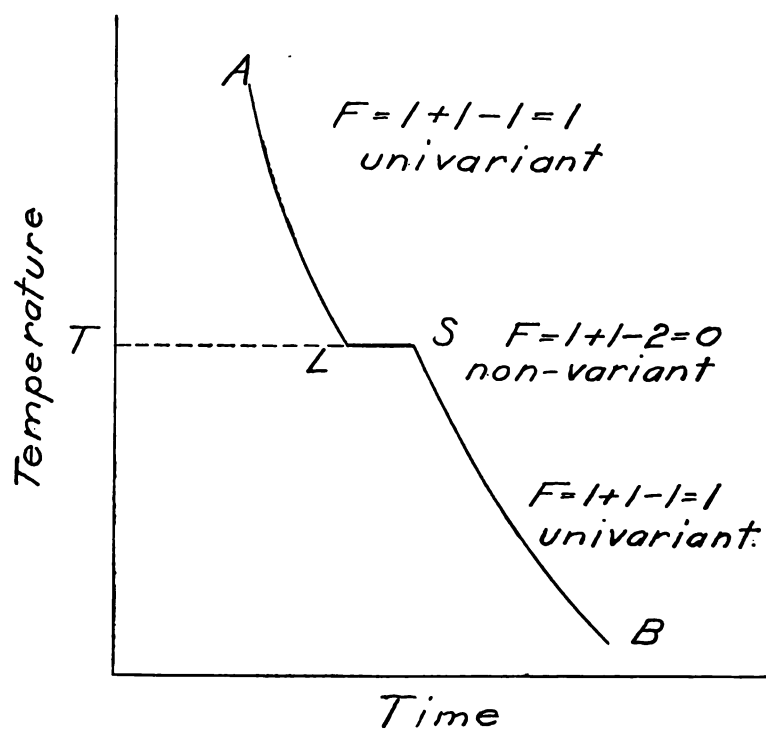

Fig. 1. — Equilibrium of pure metals according to the Phase Rule.

equilibrium: it remains liquid. At the temperature T two phases are present, solid metal and liquid metal, the metal having, therefore, no degree of freedom ($F = 1 + 1 - 2 = 0$): it is non-variant. Liquid and solid metal can exist only at one temperature, the critical temperature of solidification, any change of its temperature resulting in the disappearance of one of the phases, that is, in a return to stable equilibrium. Increasing the temperature must result in the disappearance of the solid phase, while lowering the temperature must cause the disappearance of the liquid phase. Below the temperature T the system contains only the solid phase, being, therefore, univariant: its temperature may be varied arbitrarily.

The Phase Rule Applied to Binary Alloys. — Binary alloys having for components the two alloying metals, the formula of the phase rule becomes:

$$F = 2 + 1 - P$$

$$\text{or } F = 3 - P$$

Clearly binary alloys when in a condition of stable equilibrium cannot have more than two phases. With one phase they will be bivariant, with two phases univariant, and with three phases non-variant. Let us apply the rule to the fusibility curves of binary alloys of metals partially soluble in each other when solid (Fig. 2). Above the liquidus MEM' there is but one phase present, namely the liquid phase, the system being, therefore, bivariant ($F = 3 - 1 = 2$), i.e. both temperature and concentration may be varied arbitrarily without upsetting the equilibrium of the system, which means, in the case under consideration, without causing its solidification. On reaching any point L of the liquidus the alloy begins to solidify, and two phases are now present, namely, solid solution and liquid alloy, the system becomes univariant ($F = 3 - 2 = 1$). Having but one degree of freedom only the temperature or the concentration may be

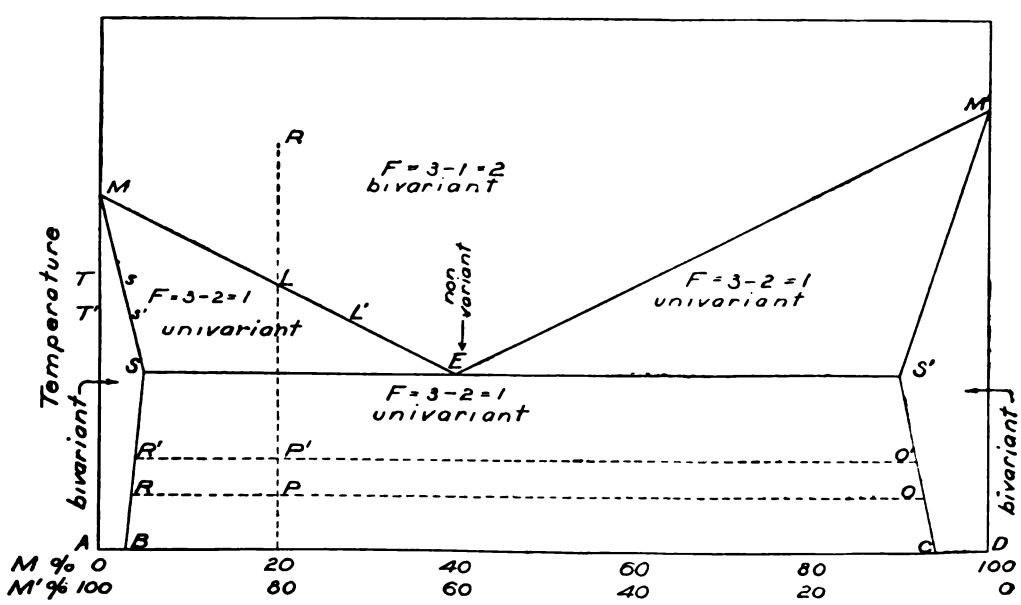

Fig. 2. — Equilibrium according to the Phase Rule of binary alloys whose component metals are partially soluble in each other in the solid state.

arbitrarily varied. Should we, for instance, lower the temperature of alloy R from T to T' (Fig. 2) the composition of the liquid phase *necessarily* shifts from L to L', and that of the solid phase in equilibrium with it from s to s'. In the region $MSES'M'$ of the diagram bounded by the liquidus and solidus lines, therefore, the alloys are univariant, any arbitrary change of temperature resulting in a well-defined change of concentration and vice versa. At E, corresponding to eutectic composition and eutectic temperature, three phases are present, namely two solid solutions and liquid alloy, the system having no degree of freedom ($F = 3 - 3 = 0$). Neither the temperature nor the concentration may be altered without causing the disappearance of at least one of the phases. Increasing the temperature must result in the disappearance of both solid solutions, the system becoming bivariant, while lowering it must be followed by the disappearance of the liquid phase. Again, shifting the concentration to the left or right of E must yield the univariant system solid solution plus liquid. Clearly two solid phases and a liquid phase can only exist at one critical temperature and for one critical composition of the alloy; in the case of a eutectic

alloy these three phases can exist only at its freezing temperature. In the areas *AMSB* and *DM'S'C* single homogeneous solid solutions only are present, that is, but one phase exists, and the corresponding alloys have, therefore, two degrees of freedom. Arbitrary changes both of temperature and composition within these areas do not disturb the equilibrium of the system. Within the region *BSS'C* two phases occur, solid solution *M* and solid solution *M'*, the corresponding alloys having, therefore, but one degree of freedom. Increasing the temperature from *P* to *P'*, for instance, must result in shifting the composition of the solid solutions respectively from *R* to *R'* and from *O* to *O'*.

The Phase Rule Applied to Iron-Carbon Alloys. — Since iron-carbon alloys belong to the class of binary alloys the constituents of which are partially soluble in each other in the cold, the application of the phase rule to their equilibrium diagram should not present any difficulty, but we have now to consider allotropic changes as well as changes of state. Their possible phases or metarals are: (1) liquid iron, (2) liquid solution of carbon (or Fe_3C) in iron, (3) solid solution (austenite) of carbon (or Fe_3C) in gamma iron, (4) solid gamma iron, (5) solid beta iron, (6) solid alpha iron (ferrite), (7) solid solution (martensite)[1] of carbon (or Fe_3C) in beta iron, (8) solid cementite, (9) graphite, and possibly others. The exact nature of troostite and sorbite being still in doubt, they are not here classified as phases, seeing that they may be, and probably are, aggregates of two or more phases, unless indeed they be, according to Benedicks, emulsions or colloidal solutions. Scientists do not agree, however, as to whether colloidal solutions are or are not phases, opinions differing in regard to their homogeneity. Indeed some writers like Le Chatelier question the existence of colloidal solutions which they consider as finely divided aggregates. Pearlite evidently is not a phase, but an aggregate of the two phases, ferrite and cementite, in constant proportion after the fashion of eutectic and eutectoid mixtures.

Let us now apply the teachings of the phase rule to the iron-carbon equilibrium diagram (Fig. 3). The number and kinds of phases existing at different temperatures, and for different proportions of the components, iron and carbon, have been clearly indicated and will be readily understood in view of the foregoing considerations. Above the liquidus *LEL'* all alloys are composed of but one liquid phase, and have, therefore, two degrees of freedom; between the liquidus and solidus, that is, in the region *LSE* and *L'S'E*, two phases are present, liquid solution plus solid solution (austenite), or liquid solution plus solid Fe_3C, hence the corresponding alloys have here but one degree of freedom; alloys of composition *E* and at the corresponding temperature are evidently made up of three phases, namely liquid solution plus solid austenite plus solid cementite, being, therefore, non-variant; in the region *LADS* all alloys being composed of but one phase, namely, solid austenite, are bivariant; at *D* the alloy contains three phases, ferrite, cementite, and austenite, and is, therefore, non-variant; in the area *DSS'F* two phases are present, solid solution (austenite) plus cementite, and the system has but one degree of freedom. If, as is often the case, cementite is in this region decomposed into iron and graphite the alloys are for the time being non-variant, becoming again univariant on the complete disappearance of cementite. In the region *ABH* beta iron and austenite are present, the alloys having in consequence but one degree of freedom; in the region *BCDH* alpha ferrite and austenite are present and the alloys, therefore, are univariant. Finally below *CDF* three possible cases should be considered: (I) the cementite formed during solidification and subsequent cooling

[1] All investigators do not agree as to the homogeneity, that is the phase-like character of martensite, some still regarding it as an aggregate.

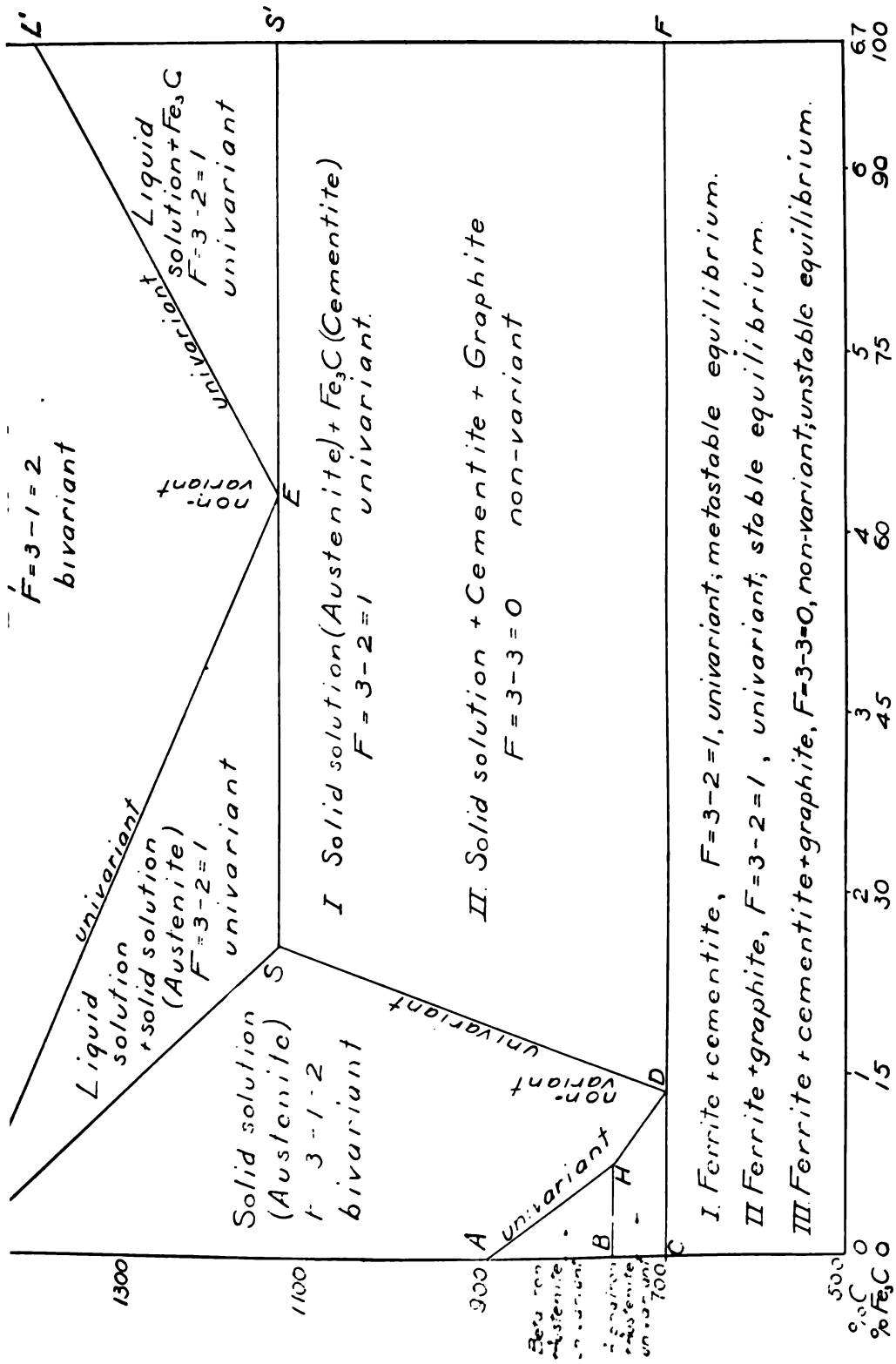

Fig. 3. — Equilibrium of iron-carbon alloys according to the Phase Rule.

remains unchanged, in which case the alloys are made up of the two phases ferrite and cementite, being, therefore, univariant, their equilibrium, however, as previously explained, is supposed to be metastable; (II) the cementite has been completely converted into ferrite and graphite, only those two phases being present, undoubtedly representing the stable equilibrium of all iron-carbon alloys; (III) the dissociation of cementite has been incomplete, both cementite and graphite being present, which with ferrite give three phases, the corresponding alloys being non-variant and, therefore, their equilibrium unstable. Condition (I) generally prevails in all grades of steel, and is readily produced in cast iron by rapid cooling especially in the absence of considerable silicon, the resulting alloys being known as white cast iron. Condition (II) never obtains in steel, but may be produced in highly carburized alloys by very slow cooling through and below solidification, especially in the presence of much silicon and in the absence of manganese and sulphur. Condition (III) is the condition of the gray cast irons of commerce, their compositions and other influences prevailing during their cooling being such as to cause the graphitizing of varying proportions of cementite.

Examination

Describe the application of the phase rule to iron-carbon alloys containing respectively 0.60, 1.25, 3.00, and 5.00 per cent carbon as they cool from the molten condition to atmospheric temperature.

APPENDIX I

MANIPULATIONS AND APPARATUS

In the foregoing pages the author has described at length those apparatus and manipulations which in his laboratory he has found to yield the best results. In the present appendix the apparatus and manipulations of some other workers are briefly described.

POLISHING AND POLISHING MACHINES

Sorby in his pioneer work polished his samples on emery-papers of increasing fineness followed by rubbing with tripoli, crocus, or Water-of-Ayre stone, and finally with jeweler's rouge. Emery-papers are still used, but for quick polishing they are often replaced by emery-powders spread wet on revolving wheels; the author has retained the use of tripoli powder for the treatment preceding the final polishing but others now prefer specially prepared flour-emery or diamantine; jeweler's rouge is still widely used for the final treatment, although some prefer specially prepared alumina, as first suggested by Le Chatelier.

In 1904 Osmond's polishing method consisted in roughing off with emery and polishing with rouge. Emery-papers of increasing fineness were stretched over glass plates. The papers used were prepared by mixing with water levigated "120 minutes" emery[1] and collecting the deposits formed at the end of increasing periods of time in precipitating glasses. The classified powders, after drying, were mixed with a mucilage of albumen (made up of 72 cubic centimeters of albumen and 28 cubic centimeters of water beaten to a froth and, after 12 hours, strained through a fine-meshed sponge) and spread on paper of the best quality. Osmond also prepared his own rouge by calcining copperas at as low a temperature as possible and separating the finest product by levigation. The rouge was spread on a piece of cloth stretched over the cast-iron table of a small horizontal polishing machine and used wet.

In 1900 Le Chatelier's method of polishing specimens of iron and steel previously rubbed upon emery-papers, including the finest grades, consisted in rubbing them successively (1) on emery-paper prepared with albumen, according to Osmond, with the deposit obtained in between a quarter of an hour and one hour in the ammoniacal washing of flour-emery, (2) on a felt disk covered with some soap paste prepared with the deposit of alumina or of emery, obtained in between one and three hours, (3) on a flat disk made of wood, metal, or ebonite, covered with cloth, velvet, or leather strongly glued upon it; upon this covering the soap preparation, obtained with the deposit of alumina after twenty-four hours, was spread. The last two disks

[1] By "120 minutes" emery is meant emery which has taken 120 minutes to settle in a vessel of water of certain dimensions.

were rotated by some mechanical devices producing great speed. All disks must be frequently moistened with a brush or sponge.

According to Gœrens, Le Chatelier's method in 1908 consisted in the use of (1) small sheets of French emery-paper, Hubert grades IG and 00 on ground glass plates, (2) flannel stretched over glass covered with "one minute" emery previously passed through a fine sieve (1200 meshes per sq. cm.), some soap solution being also poured over the cloth, (3) a similar support covered with "120 minutes" emery previously passed through a very fine sieve (2600 meshes per sq. cm.) and washed, and (4) a vertically revolving brass disk covered with flannel and washed alumina. The fine alumina mixed with water and soap solution may be sprayed on the disk by means of the sprayer shown in Figure 1.

The preparation of fine alumina powder for the final polishing of iron and steel

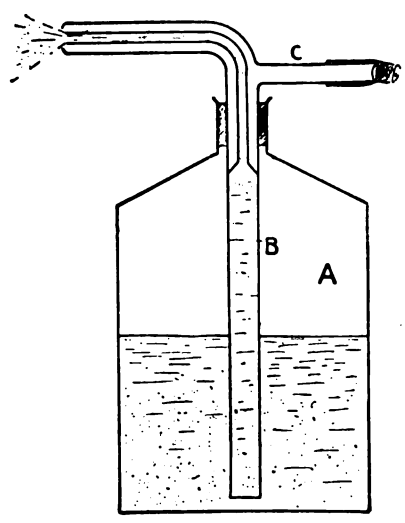

Fig. 1. — Sprayer for emulsified alumina. (Gœrens.)

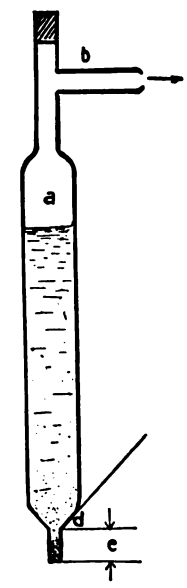

Fig. 2. — Pipette for the levigation of alumina. (Gœrens.)

samples was first described by Le Chatelier in 1900. The method used is that employed by Schlœsing for the analysis of kaolins. The following description of Le Chatelier's manipulation is from Gœrens (1908).

The purest precipitated alumina, from ammonia alum, is passed through a sieve of 2600 meshes per sq. cm., and 100 grains of it in 300 c. c. of distilled water are triturated in a mill for three hours. The whole is then poured into a liter flask, well shaken, and about 200 c. c. pipetted off into a flask closed with a rubber stopper. To this are added 1800 c. c. of distilled water and 2 c. c. of concentrated nitric acid (1.4 sp. gr.), the mixture well shaken, and allowed to settle; the settling is complete in a short time (about two hours). The clear supernatant liquid is siphoned off with an S-shaped siphon; with careful manipulation this is possible to the extent of $\frac{9}{10}$ of the total amount. The liquid drawn off is replaced by distilled water, the mixture well shaken several times, and allowed to settle again, after which the wash water is

again drawn off as before. This is repeated three or four times more. At last the supernatant liquid remains milky for a whole day, which is an indication of the perfect removal of acid. Finally, distilled water is added for the last time up to about 2 liters, the mixture thoroughly shaken, and the alumina separated from the liquid in the apparatus shown in Figure 2. A pipette *a* of about 500 c. c. capacity is drawn out below to an opening of about 3 mm. internal diameter. The alumina is prevented from clinging by giving an inclination of at least ⅓ to the sloping sides of the tube. The piece *b* is connected to the water pump. The end (of the pipette) is dipped into the vessel containing the emulsified alumina, and the pipette sucked full, whereupon the opening *b* is closed with a screw cap so far that one drop runs out about every fifteen seconds. The material obtained during the first quarter of an hour is very heterogeneous and still scratches the surface of the section markedly, so that it cannot be used. After a quarter of an hour has expired the tap is closed and the alumina allowed to settle completely. After three hours the material is placed in the flask *A* (Fig. 1) provided with a spraying arrangement. Soap solution[1] is added and the mixture diluted with distilled water. The material thus prepared is ready for use, and is suitable for steel and pig iron. The residue which settles in 3 to 24 hours is treated similarly, and serves for polishing softer materials (iron, copper, etc.). The portion which still remains in suspension after 24 hours is too fine and is poured away.

The same method has been applied to commercial flour-emery, oxide of chromium, and oxide of iron, but the resulting products are far from being as satisfactory as the alumina powders.

Revillon has recently described a rapid method of preparing alumina suitable for polishing. A certain amount of alumina is suspended in a large volume of water, well shaken, and allowed to stand for five minutes. The liquid is then siphoned off and with the particles of alumina still held in suspension may be used for polishing. To obtain finer powders 15 to 20 grams of finely ground alumina should be mixed with one liter of distilled water, shaken, and allowed to settle five minutes. Most of the liquid is then siphoned off, transferred into another vessel, and allowed to stand fifteen minutes; the decantation is repeated, etc., a clearer liquid, that is one holding finer particles in suspension, being obtained every fifteen minutes. The final liquid, from which no powder is deposited, may be used for the finest polishing, the intermediate products for rougher work.

Robin has described the preparation of alumina powder by a method based upon the catalytic action of mercury in causing the oxidation of pure aluminum. Strips of aluminum are immersed in mercury for a short time and then exposed to moist air when the small amount of mercury they have absorbed causes the oxidation of the metal, growth of Al_2O_3 taking place, the increase of which is visible with the naked eye. This alumina can be readily detached and as a fine powder may be used for polishing. Robin claimed for his method the advantages of greater simplicity and lower cost.

In 1900 Stead recommended for polishing iron and steel samples the use of emery-papers, Hubert grades Nos. 0, 00, and 000, followed by rubbing with one grain of diamantine powder[2] spread wet over a smooth black cloth and, for final treatment, gold rouge used dry on chamois leather or, for finer structures, wet on parchment or

[1] The soap solution is prepared by dissolving pure (Venetian) soap in hot water and filtering through a filter paper into a flask. After cooling the solution should be sirupy.

[2] Diamantine powder consists of pure alumina and is used by jewelers for polishing steel.

kid leather. He used a simple, hand polishing machine in which one block at a time was made to rotate horizontally (Fig. 3).

A foot polishing machine also designed by Stead is shown in Figure 4 and a

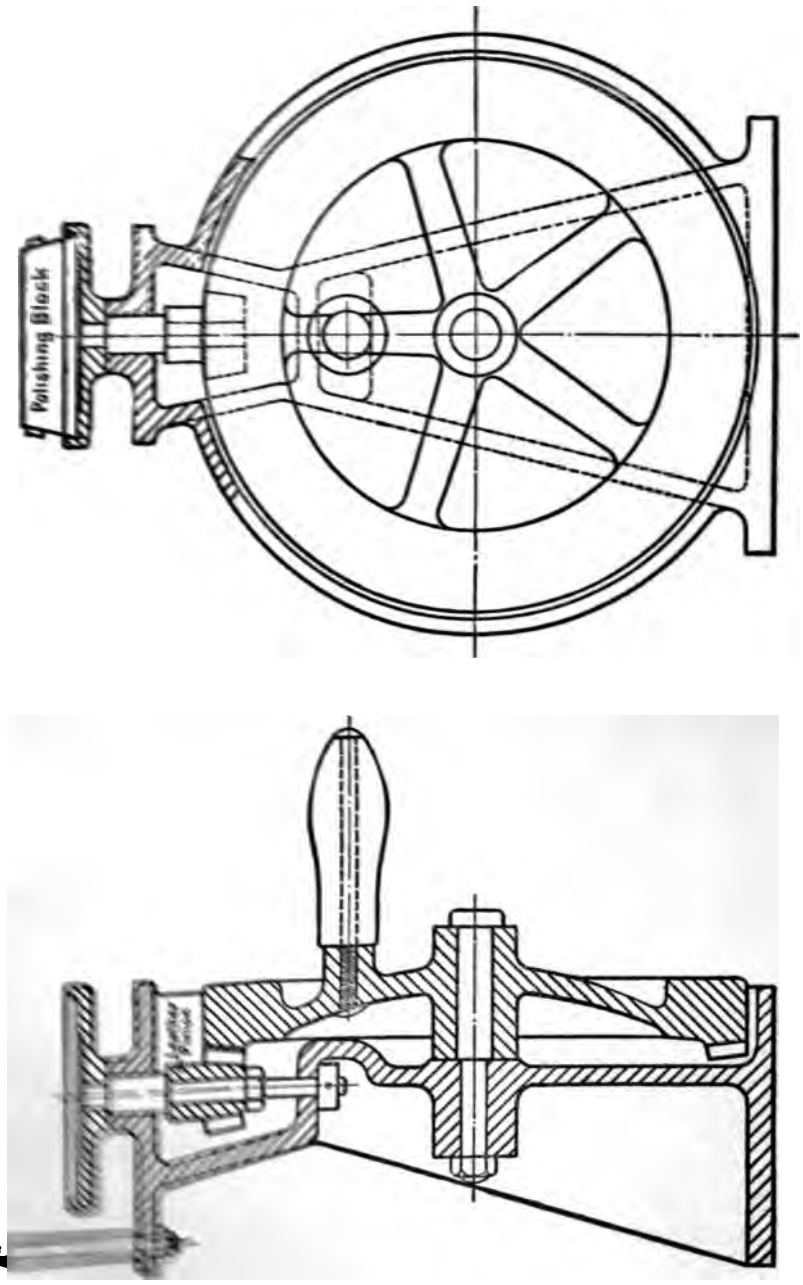

Fig. 3. — Hand polishing machine. (Stead.)

[illegible] shown in Figure 5. In these machines brass disks carrying [illegible] are attached to vertical spindles and driven from below. [illegible] of these blocks by means of brass rings slipping

over them while others are covered with cloth in a similar way. Clamps are provided for holding the samples against the revolving disks. The central vessel contains the water needed for wet polishing, a small tap projecting over each disk. The excess water is caught by brass water guards and discharged into a trough below the level of the disks. These machines are made by Carling and Sons of Middlesbrough, England.

Martens, according to Gœrens (1908), uses vertically rotating disks upon which

Fig. 4. — Foot power polishing machine. (Stead.)

Fig. 5. — Multiple polishing machine. (Stead.)

are pasted emery-papers, Hubert brand, grades 3, 2, 1G, 1M, 1F, 0, and 00 and, for final treatment, levigated jeweler's rouge on cloth. The disks make 400 revolutions per minute. The average time needed to polish a specimen varies between 1½ and 2 hours.

Gulliver (1908) recommends for polishing the use of emery-papers grades No. 1, 0, and 00 on hard wood or plate glass and for final treatment the finest rouge or diamantine powder on cloth stretched over hard wood.

The polishing machines shown in Figures 6 and 7 are made by P. F. Dujardin of Düsseldorf. It will be noted that one side only of the disks is utilized. A machine like the one of Figure 7 is also made for belt driving.

Sexton describes the polishing machine Figure 8, made by Baird and Tatlock. Its construction is obvious.

A simple polishing machine consisting of an horizontally revolving disk (Fig. 9) was described in 1899 by Ewing and Rosenhain. *A* is the spindle of an electric motor carrying a small driving disk *B*, fitted with a rubber ring to increase the driving fric-

Fig. 6. — Foot power polishing machine. (P. F. Dujardin and Co.)

tion. The polishing disk *C* has a vertical axis running in a bearing on the casting *D*. The under side of the polishing disk bears upon the driving wheel *B* and takes motion from it.

A. Kingsbury in 1910 described his polishing method. He prepares his supporting blocks by pouring paraffin on brass disks. After solidifying these paraffin blocks which are about ½ inch thick and 8 inches in diameter have their upper face dressed flat. They are made to rotate horizontally in a suitable machine and upon them emery of increasing fineness and finally rouge are used in succession. The

speed of the polishing machine is 200 revolutions per minute. The time needed to polish a sample of ordinary steel is given as fifteen minutes.

C. Campbell in 1902 described the polishing operation as consisting in rubbing the sample, previously filed smooth, successively on emery-cloth, grades 0 and 00, and on French emery-papers, grades 0, 00, 000, and 0000. The specimen is then polished on

Fig. 7. — Polishing motor. (P. F. Dujardin and Co.)

broadcloth or chamois leather with well washed rouge and water. Some workers, the writer says, use an intermediate stage with diamantine powder.

C. H. Risdale in 1899 described his polishing operation as consisting in (1) rough filing, (2) fine filing, (3) rubbing with rough commercial emery-cloth stretched on a board, (4) rubbing with fine emery-cloth stretched on a board, (5) rubbing on fine specially prepared paper on disks of Stead's polishing machine, (6) rubbing on diamantine on cloth stretched on disks of Stead's machine, (7) rubbing on rouge on

washed leather similarly mounted or, for very fine work, on rouge on wetted parchment.

Guillet in 1907 recommended for polishing two carborundum wheels and two suitably selected emery-papers and, for final treatment, alumina on cloth stretched over a revolving disk. He places smooth sheets of zinc between the wooden disks of his polishing machines and the polishing cloths.

In 1901 Arnold described as follows a quick polishing and etching method: "Take

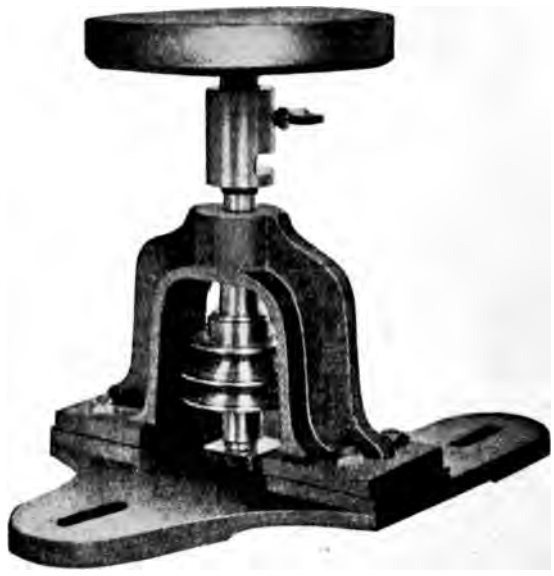

Fig. 8. — Polishing machine. (Baird and Tatlock.)

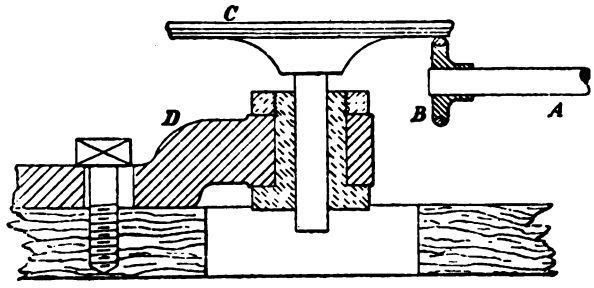

Fig. 9. — Polishing machine. (Ewing and Rosenhain.)

two pieces of hard wood, 12″ × 9″ × 1″, planed dead smooth on one side; then by means of liquid glue evenly attach to the smooth faces two sheets of the London Emery Works Co's atlas cloth No. 0. Allow the glue to set under strong pressure. Next, by means of a smooth piece of steel, rub off from one of the blocks as much as possible of the detachable emery. This is No. 2 block, the other, necessarily, No. 1 block.

"The steel section, say ⅛ inch thick and ½ inch diameter, is rubbed for one minute

on No. 1 block, the motion being straight and not circular; then, for the same time and in the same manner rub on No. 2 block. Next place the bright but visibly scratched sections in a glass etching dish 3″ × 1″ × ½″, and cover the steel with nitric acid sp. gr. 1.20.

"Watch closely until in a few seconds the evolved gases adhering to the section change from pale to deep brown and effervescence ensues. Then, under the tap, quickly wash away the acid and for a minute immerse the piece in a second dish containing rectified methylated spirits. Dry the section by pressing it several times on a soft folded linen handkerchief, when it will be ready for examination. The structure will be clearly exhibited, the innumerable fine scratches visible before etching having virtually vanished."

DEVELOPMENT OF THE STRUCTURES

The methods which, in common with many workers, the author has found most satisfactory for revealing the structure of polished iron and steel specimens have been described in these pages. They include etching with concentrated nitric acid, with very dilute alcoholic solutions of nitric acid and of picric acid (Lesson III), with sodium picrate and ammonium oxalate (Lesson V), and with the Kourbatoff reagent (Lesson XIII). Other methods have been used that should be mentioned.

Polishing in Relief. — So-called relief polishing has been used successfully by Sorby, Martens, Behrens, and especially by Osmond. It consists in rubbing the specimen on a soft, yielding support with some suitable polishing powder, the softest constituents being, so to speak, dug out, leaving the harder ones standing in relief. These differences of level make it possible to distinguish the constituents under the microscope without further treatment. It is evident that only those samples which are made up of constituents differing much in hardness can be so treated. The free cementite of hyper-eutectoid steel or of white cast iron, for instance, can be made to stand strongly in relief because it is so much harder than the accompanying pearlite or other constituents.

Osmond polishes his samples on a damp piece of parchment stretched over a piece of well-planed wood. It is sprinkled with rouge which is rubbed strongly on the parchment. The block is then put under the tap and washed so that only those particles of rouge that have found their way into the pores of the parchment are retained. To distinguish between raised portions and cavities the luminous rays are strongly diaphragmed and the objective placed a little below the focusing point, is slowly raised. The reliefs, which at first appear brilliant and yellowish on a relatively darker ground, gradually become dark on a bright ground; the cavities present inverse appearances so perfectly that two photographs of the same preparation, taken one a little below and the other a little above the mean focusing point, are almost positive and negative to one another.

Polish-Attack. — For many years Osmond obtained his best preparations by a combined polishing and etching method (*polissage-attaque*) consisting in rubbing the polished sample upon a piece of parchment covered with some aqueous extract of liquorice root, with the addition of precipitated calcium sulphate. In 1899 Osmond and Cartaud recommended replacing the extract of liquorice by a diluted solution of nitrate of ammonium (2 parts by weight of the crystallized salt to 100 parts of water). A piece of parchment spread tightly over a smooth board is soaked with the

solution and the specimen rubbed upon it until sufficiently etched. It is not necessary to add any sulphate of calcium.

Etching. — Sorby etched his specimens with very dilute solutions of nitric acid in water and this reagent was widely used for many years by other metallographists. The water has now been replaced by absolute alcohol (Lesson III, page 7). Le Chatelier has mentioned the use of glycerine as a satisfactory non-oxidizing vehicle for nitric as well as for picric and hydrochloric acid.

Osmond, the author believes, was the first to use tincture of iodine. This tincture is applied in the proportion of one drop per square centimeter of surface and allowed to act until it is decolorized, the treatment being repeated after examination if needed. Le Chatelier recommends applying the tincture with the tip of the finger and gently rubbing the specimen.

Stead uses a solution made up of 1.25 grains of iodine, 1.25 grains of iodide of potassium, 1.25 grains of water and alcohol to make up 100 c. c. After the iodine has lost its color the sample should be washed in water, then in alcohol, and finally dried in a blast of hot air.

Martens and Heyn in 1904 recommended the use (1) of an etching solution containing one part of hydrochloric acid (1.19 sp. gr.) and 100 parts of absolute alcohol,

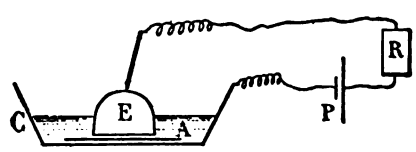

Fig. 10. — Arrangement for electrolytic etching.

and (2) of one part of hydrochloric acid in 500 parts of water with the assistance of the electric current.

Heyn used a solution of double chloride of copper and ammonium containing 12 grains of the salt and 100 grains of distilled water.

To distinguish with certainty between iron phosphide and cementite, Matweieff recommends *neutral* sodium picrate washed several times with distilled water to eliminate the excess of picric acid or of sodium that might be present. The sample is immersed in the boiling solution for 20 minutes, a treatment by which the iron phosphide is strongly attacked while the cementite and pearlite remain unaffected.

For etching austenite and martensite Robin recommends the use of a saturated solution of picric acid in alcohol, an immersion of thirty seconds to one minute, washing with water without touching the specimen and drying by air blast or simply in air. Films of various tints are formed, ferrite remaining uncolored.

Le Chatelier has used bitartrate of potassium as an etching reagent. It leaves cementite and pearlite uncolored, while it imparts a dirty coloration to ferrite.

The same author has described the use of a freshly prepared reagent made up of equal parts of a solution containing 50 per cent of soda and of a solution containing 10 per cent of lead nitrate. Cementite is quickly colored by it while the phosphides and especially the silicides are also attacked. The reagent is recommended for highly carburized metals. Medium high carbon steels of great purity are not affected by this solution, but when impure, the pearlite is energetically acted upon, probably because of the presence of impurity in that constituent.

Le Chatelier has also mentioned the use of a solution of 10 per cent gaseous hydrochloric acid in absolute alcohol to which is added 5 per cent of cupric chloride for annealed steels and one per cent of the same salt for hardened steels. Ferrite and cementite are not colored, martensite very little, austenite a little more, troostite and sorbite decidedly.

Hilpert and Colver-Glauert have described the use of sulphurous acid for non-pearlitic steels and for pig iron. A saturated solution of sulphur dioxide in water is prepared and 3 or 4 per cent of that solution in water used. The time of etching varies between seven seconds and one minute. Alcohol may be substituted for water in which case the etching lasts several minutes. The treatment causes the deposition of layers of iron sulphide of different thickness and, therefore, of different colors, on the various constituents.

Electrolytic Etching. — Le Chatelier was one of the first to advocate the use of the electric current in order to obtain a more uniform action in etching iron and steel samples. Sheet lead may be used for the positive electrode, and, as electrolyte, a 10 per cent solution of chloride or sulphate of ammonium gives good results. The current needed varies between 0.001 and 0.01 amperes per square centimeter.

Electrolytic etching has been described by Cavalier (1909). A few cubic centimeters of the electrolyte are placed in a platinum dish *C* (Fig. 10) connected with one pole of the battery *P*; the specimen *E* connected with the other pole is placed in the solution, a piece of filter paper *A* being inserted between the dish and the polished surface of the specimen. The current is regulated through the rheostat *R*. Four or five volts are required with an intensity of 0.001 to 0.01 amperes per square centimeter. The attack lasts from a few seconds to a few minutes.

Heat Tinting. — Heat tinting as a means of imparting different appearances to the various constituents of iron and steel was first used by Behrens and Martens and later, with much success, by Stead. When a polished piece of iron or steel is heated in an oxidizing atmosphere oxidized films are formed, the color of which varies with the thickness, that is, with the temperature and duration of treatment. It is also found that the various constituents are differently colored because oxidized at different speeds. According to Stead the metal should be first well rubbed with a piece of linen or chamois leather and placed on an iron plate heated by a Bunsen burner. It is best to heat gradually and examine periodically under the microscope and stop when the structure appears to be most perfectly colored. After each heating the section may be placed in a dish of mercury so as to cool it rapidly and check further oxidation. The oxidized films assume in succession the following tints as they increase in thickness: pale yellow, yellow, brown, purple, blue, and steel gray. The method is especially useful for identifying phosphides, sulphides, and carbides in cast iron and for detecting the more highly phosphorized portions of iron and steel. Free cementite colors less readily than iron but more rapidly than phosphide of iron. Iron containing phosphorous in solid solution colors more rapidly than pure iron or than iron containing less phosphorus.

Hot Etching. — Steel while at a high temperature (red heat) has been etched (1) by Saniter in molten calcium chloride heated to the desired temperature, and (2) by Baykoff in a current of gaseous hydrochloric acid.

Washing and Drying. — After removing the specimens from the etching bath, the author washes them in alcohol and dries them in an air blast. They are then rubbed once or twice *very gently* on a block covered with a fine piece of chamois skin and

carefully kept free from dust. Washing in water, in caustic potash, in lime water, and in ether has also been recommended as well as the use of fine linen cloth and of a hot blast for drying.

Preserving. — The author preserves his etched specimens in dessicators and in air-tight cabinets.

Several protective coatings have been described. Stead covers them with paraffin wax dissolved in benzole, which is removed by wiping with a clean linen rag moistened with benzole, when it is desired to examine the specimens. Le Chatelier applies a coating of "zapon," a solution of gun cotton in amyl acetate sufficiently transparent to allow examination with the highest powers.

By keeping the specimens in mercury their tarnishing should be effectively prevented while they would be at all times accessible for immediate examination. Nor should this scheme call for the use of a large amount of mercury nor for much space; flat glass trays might be used containing just enough mercury to cover their smooth bottom and the specimens placed in them polished face down. In this way a large

Fig. 11. — Stead's mounting device. (C. H. Desch's Metallography.)

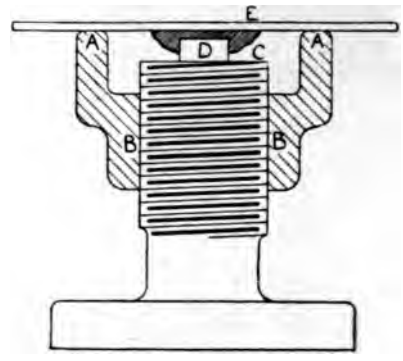

Fig. 12. — Gulliver's mounting device.

number of samples could be preserved in a small place and in a small quantity of mercury. In a tray measuring 12 by 12 inches, for instance, nearly 200 samples of ordinary size (½ to ¾ inch in diameter) could be kept.

MOUNTING AND MOUNTING DEVICES

The author's special holders for placing the prepared samples on the stage of the microscope have been described (see Apparatus for the Metallographic Laboratory, page 7). Other methods have been used and are still employed by some workers, namely (1) mounting in some plastic material, and (2) the use of leveling stages.

Plastic Mounting. — Osmond mounts his specimens by embedding them in a little soft wax placed upon a glass plate. The leveling is managed by means of two pieces of glass tube of equal height, one on each side of the sample.

Stead places the specimens polished face down on a piece of plate glass (Fig. 11) and surrounds them with brass cylinders accurately turned. A piece of plastic wax is stuck upon the center of a glass microscope slide and is then pressed upon the section till the glass slide comes in contact with the brass ring. The specimen adheres to the wax and the mounting is complete.

Gulliver (1908) describes the device (Fig. 12) for mounting specimens. It consists

of a circular ring faced on its upper surface *A*, and screwed internally at *B* to fit the foot, of which the upper end *C* is also faced. The distance between the parallel faces *A* and *C* can thus be adjusted. The specimen is placed at *D* and a glass slide *E* with some soft modeling clay or wax is pressed upon it until the glass touches the ring at *AA*.

Mechanical mounting devices working on the principle of the microtome have also been used. They have been described by M. A. Richards: "Projecting from a cylindrical metal base three inches in diameter, is a threaded upright three and one-

Fig. 13. — Watson and Sons' mounting device.

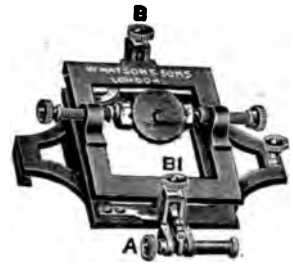

Fig. 14. — Watson and Sons' leveling stage.

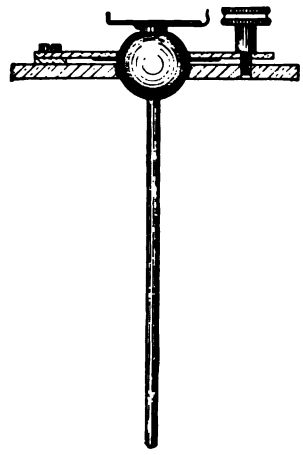

Fig. 15. — Huntington's leveling stage.

half inches in diameter. A cylindrical nut or collar three inches high and two and one-half inches outside diameter screws on the threaded upright. A small circle of chamois skin is placed on the top of the thread upright to protect the etched face of the micro-section. To mount a section, place it face down on the chamois skin, press upon the upper projecting portion a lump of beeswax, and upon this place the ground glass (ground surface down). A few revolutions of the collar will cause the glass to rest upon the upper edge of the collar, and the adhesion of the glass and beeswax to the specimen may be made complete by slowly turning the collar down with one hand while keeping the glass base in close contact with the collar-top with the other hand. In this manner, no matter how irregular the section, the parallelism of the etched surface and the glass base may be very quickly and accurately obtained."

The mounting device (Fig. 13) is constructed by Watson and Sons. It consists of two horizontal plates, the upper one being capable of vertical movement but always remaining parallel to the lower one. The specimen is placed with its polished surface on the lower plate, and the upper plate carrying a glass slip to which some suitable clay or wax is attached is lowered into contact.

Leveling Stages. — The leveling stage (Fig. 14) is constructed by Watson and

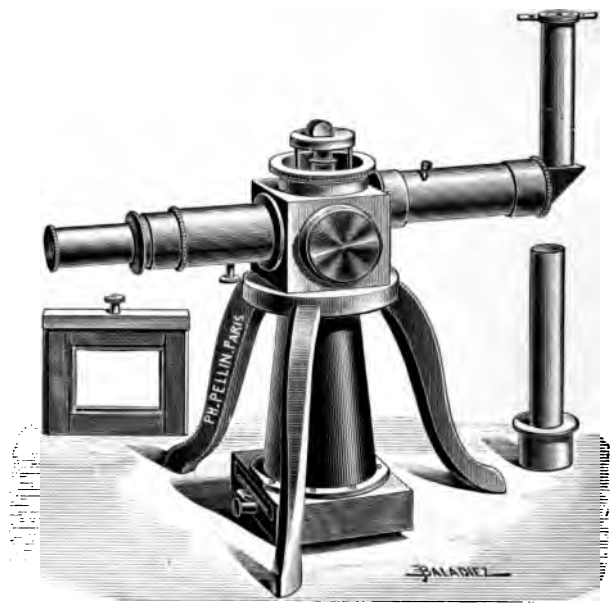

Fig. 16. — Le Chatelier's inverted metallurgical microscope. Early form.

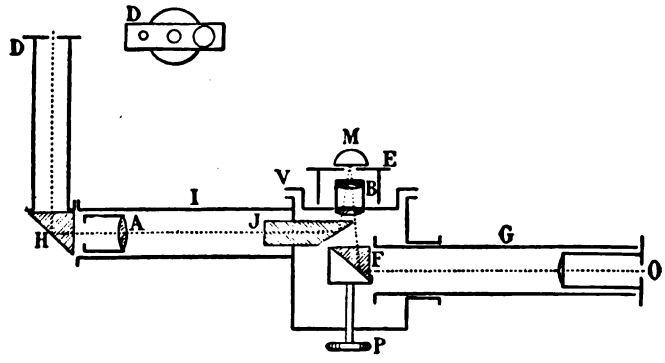

Fig. 17. — Le Chatelier's inverted metallurgical microscope.

Sons, London. The specimen is held by two rotating jaws and can be leveled by means of the screws *A* and *B BI*.

Professor A. K. Huntington devised the leveling stage shown in Figure 15. It is provided with a ball and socket joint for leveling, permitting the placing of the sample in any position.

Other forms of leveling stages are shown in some of the illustrations in the following pages as part of some metallurgical microscopes.

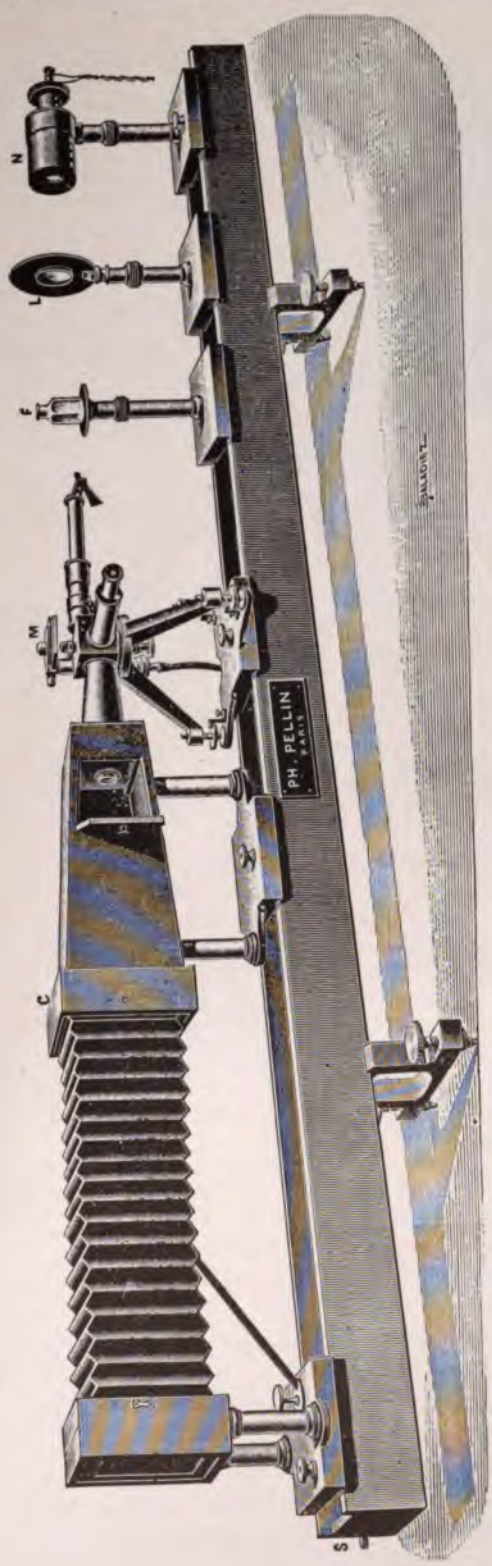

Fig. 18. — Le Chatelier's inverted metallurgical microscope.

METALLURGICAL MICROSCOPES

The microscopes and accessories used by the author have been fully described. In the following pages instruments used by some other workers or described by them, as well as those manufactured by well-known makers, are mentioned.

Le Chatelier. — In 1897 Le Chatelier devised an inverted microscope which later

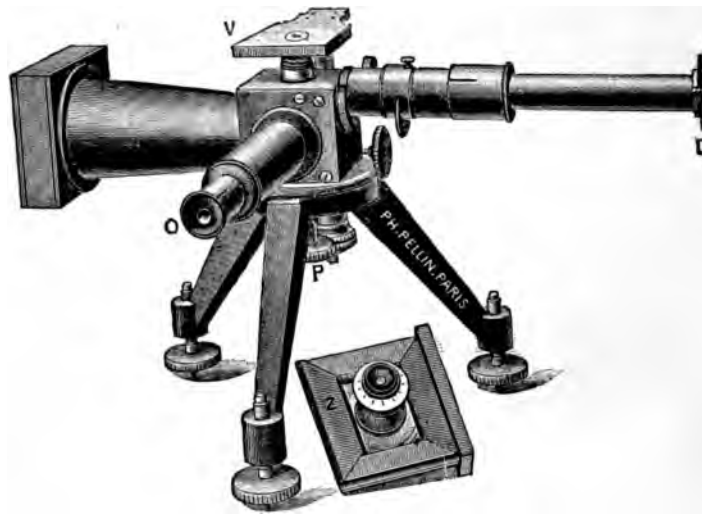

Fig. 19. — Le Chatelier's inverted metallurgical microscope.

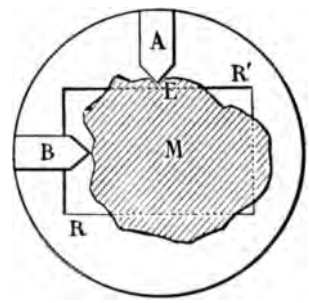

Fig. 20. — Device for placing specimens on the stage of the Le Chatelier microscope in a fixed position. (Le Grix.)

he greatly improved and which is now constructed with unimportant modifications by several microscope makers. An early form of Le Chatelier's instrument is shown in Figure 16 and its more recent construction in Figures 17 and 18. The objective *B* (Fig. 17) is directed upwards while the eye-piece *O*, placed horizontally, receives the image by the reflection of a totally reflecting prism *F* placed below the objective. The prism *F* may be rotated by means of the milled head *P* and the light reflected by the objective turned at will into the tube *G* and the eye-piece *O* for visual examination

or into another tube connected with a camera for photographing (Fig. 18). The light is condensed by the lens *A* and, being deflected at right angles by the prism *J*, passes through the objective *B* and reaches the object *M* placed on the stage *E*. In case the light is placed at a higher level than the condensing lens *A*, it must be received by a totally reflecting prism *H* which directs it into the condenser *A*. *D* is a diaphragm placed at the principal focus of the complex optical system composed of the objective *B*, the illuminating prism *J*, and the lens *A*. The opening as well as the position of the diaphragm may be altered. Another diaphragm placed at *I* affords a means of stopping the light which would fall upon parts of the preparation outside of the portion examined and which would increase the blur resulting from the reflection of useless rays by the back lenses of the objective. In the early construction of this instrument when the object was to be photographed the prism *F* was withdrawn from the path of light and the image allowed to form on a photographic plate placed *below* (Fig. 16).

A slightly different construction is shown in Figure 19. For photographic purposes the image forms on a plate placed in a holder rigidly connected with the instru-

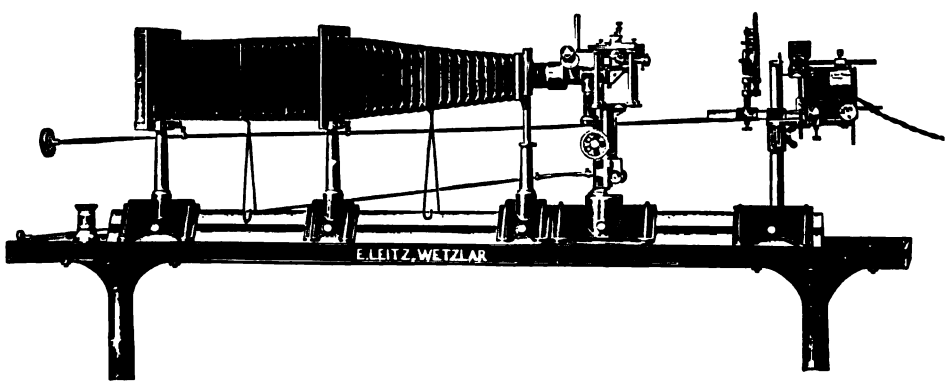

Fig. 21. — Inverted metallurgical microscope constructed by E. Leitz.

ment, no eye-piece being used. As the distance between the photographic plate and the objective is short, very small photomicrographs are obtained, which must generally be subsequently enlarged. *Z* is a plate carrying an eye-piece for use with the long bellows camera (Fig. 18). The Le Chatelier microscopes are constructed by Ph. Pellin of Paris.

In order to be able to examine identical portions of the same specimen at different times with the Le Chatelier microscope, Le Grix (1907) suggested the arrangement shown in Figure 20. A circular metallic disk with rectangular opening *RR'* and carrying two pointed stops *A* and *B* is fitted to the stage. A file mark *E* is made in the specimen *M*, which is then placed on the stage so that the stop *A* enters the groove *E* while the specimen presses against the other stop *B*, in this way securing a constant position for the object.

Ernst Leitz. — A slightly modified form (Fig. 21) of the Le Chatelier inverted microscope is made by Ernst Leitz of Wetzlar, Germany. The modifications were suggested by Guertler. The stage and illuminating appliances are shown on a larger scale in Figure 22.

The same maker also manufactures the microscope shown in Figures 23 and 24

designed by W. Campbell. The stage can be removed and the upper part of the instrument attached to the base for the examination of large surfaces.

P. F. Dujardin. — P. F. Dujardin and Co. of Düsseldorf construct a Le Chatelier

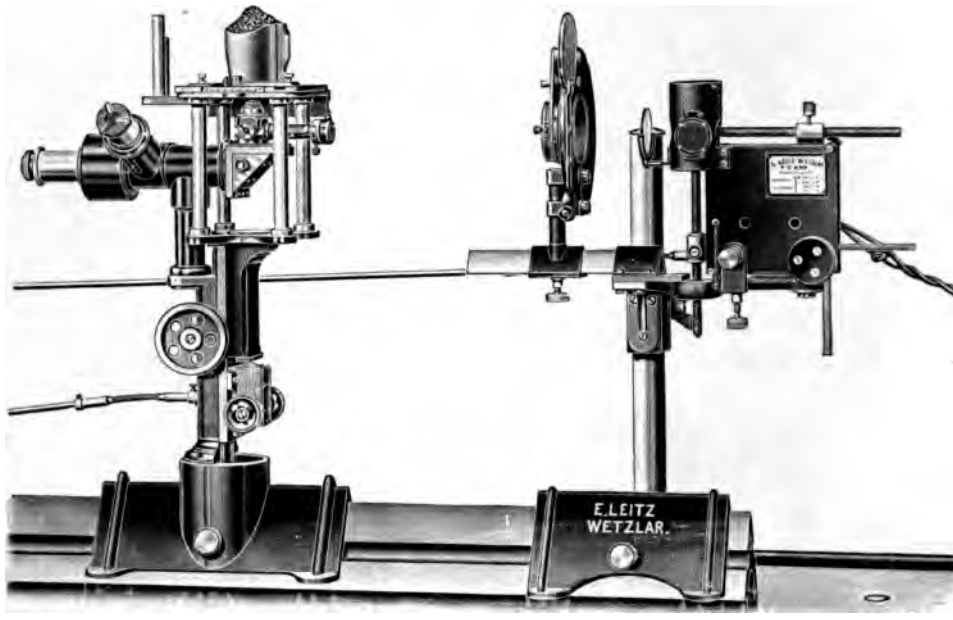

Fig. 22. — Inverted metallurgical microscope constructed by E. Leitz.

Fig. 23. — Metallurgical microscope constructed by E. Leitz.

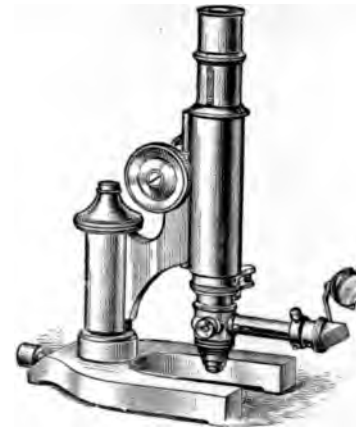

Fig. 24. — Metallurgical microscope constructed by E. Leitz.

inverted microscope as shown in Figure 25. They also make the microscope (Fig. 26) in which the vertical illuminator carries its own source of light and condenser.

C. Reichert. — The metallurgical microscope (Fig. 27) designed by Professor Rejtö is made by C. Reichert of Vienna. The position of the vertical illuminator immediately below the eye-piece should be noted. The stage is provided with a level-

ing mechanism. The same maker manufactures an inverted Le Chatelier microscope as shown in Figure 28. According to Desch, in this microscope, two right-angled prisms are cemented together to form the cube *P* (Fig. 29). The upper prism is sil-

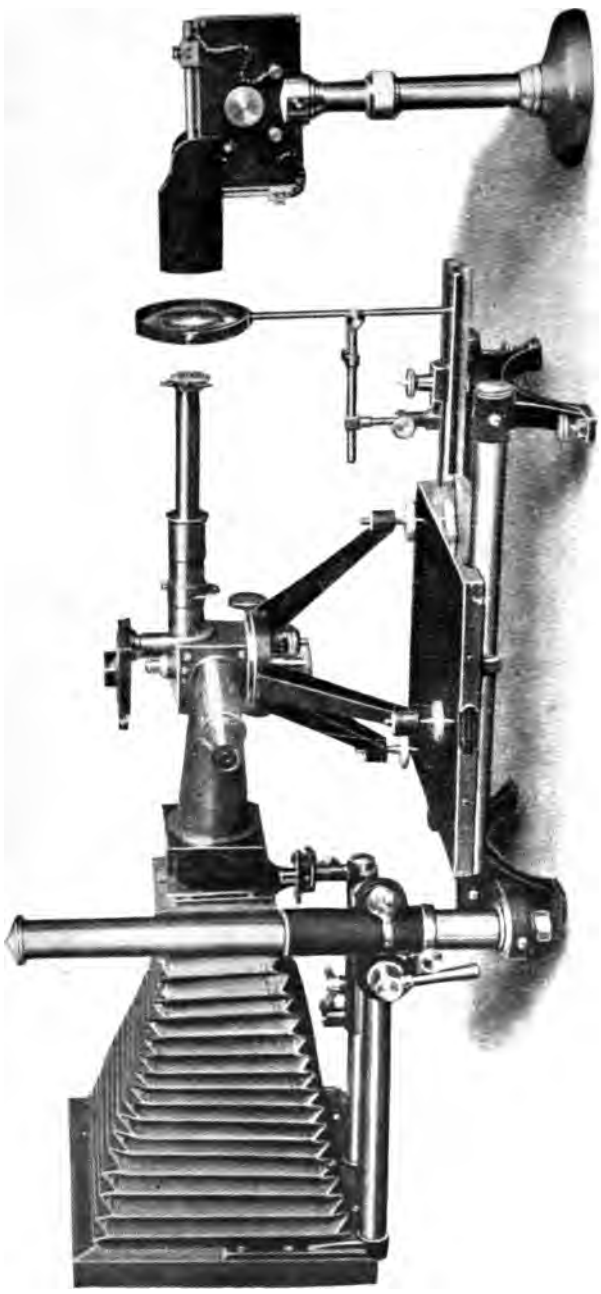

Fig. 25. — Inverted metallurgical microscope constructed by P. F. Dujardin and Co.

vered over an elliptical area, as shown by the central dark line. A portion of the light proceeding from the mirror *M* passes through the clear portion of the glass cube *P* and falls upon the object *S*. The light reflected back by the object upon striking

the silvered portion of the prism is deflected at right angles into the tube *O* which conducts it to the eye or to a photographic plate.

R. Fuess. — A metallurgical microscope practically identical in construction to the Le Chatelier inverted instrument is made by R. Fuess of Steglitz, near Berlin.

Robin. — The microscope and photographic attachment shown in Figure 30 was

Fig. 26. — Metallurgical microscope constructed by P. F. Dujardin and Co.

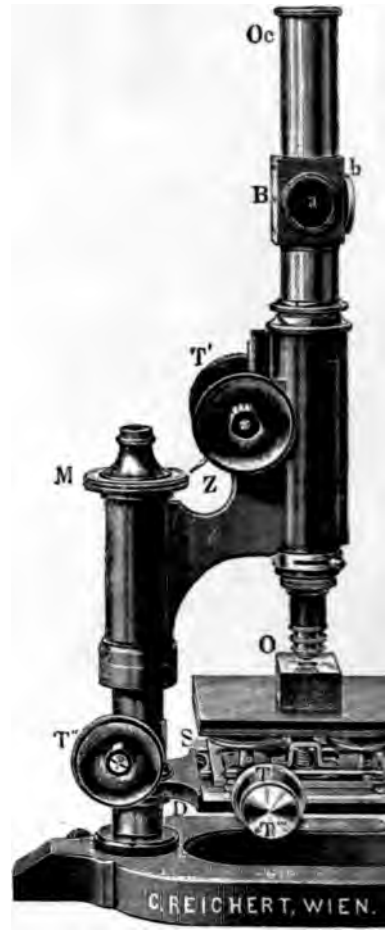

Fig. 27. — Metallurgical microscope constructed by C. Reichert.

designed by Robin. Visual examination is possible only on the screen of the camera. The stage consisting of a smooth disk is tilting and the specimen is fastened upon it with wax. To secure an accurately horizontal position of the polished surface, a plug with a perfectly flat surface is screwed into the microscope in place of the objective and the stage raised until the specimen coming in contact with the plug, the latter through gentle pressure causes the polished surface to assume a horizontal position. The plug is then removed and the objective inserted.

Martens. — The Martens metallurgical microscope (1899) made by Zeiss of Jena is shown in Figure 31. It can be used horizontally only, the tube is very wide and

Fig. 28. — Inverted metallurgical microscope constructed by C. Reichert.

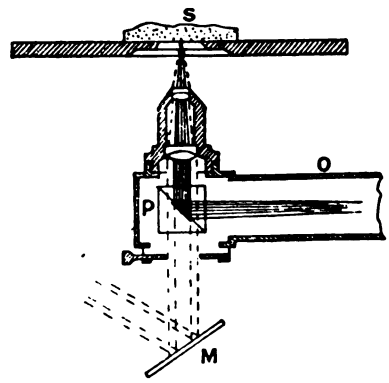

Fig. 29. — Illuminating prisms of Reichert's inverted microscope.

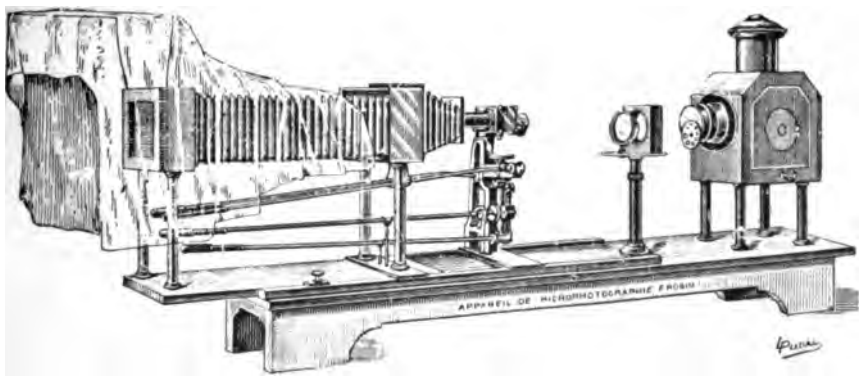

Fig. 30. — Metallurgical microscope designed by Robin.

the vertical, mechanical stage is provided with both coarse and fine adjustments *Y* and *Z* and with leveling screws *aa*. The flexible connection *f* permits the focusing

of the object from the camera screen. The instrument is designed especially for photography.

A complete Zeiss equipment including a large electric arc lamp is shown in Figure 32. It will be noted that the mounting of the camera is entirely separate from that of the other parts.

Martens also designed the ball-jointed microscope (Fig. 33) which he used principally for observing the progress of etching.

Rosenhain. — The microscope shown in Figure 34 was constructed by R. and J. Beck for Rosenhain. The stage is mechanical and provided with coarse and fine

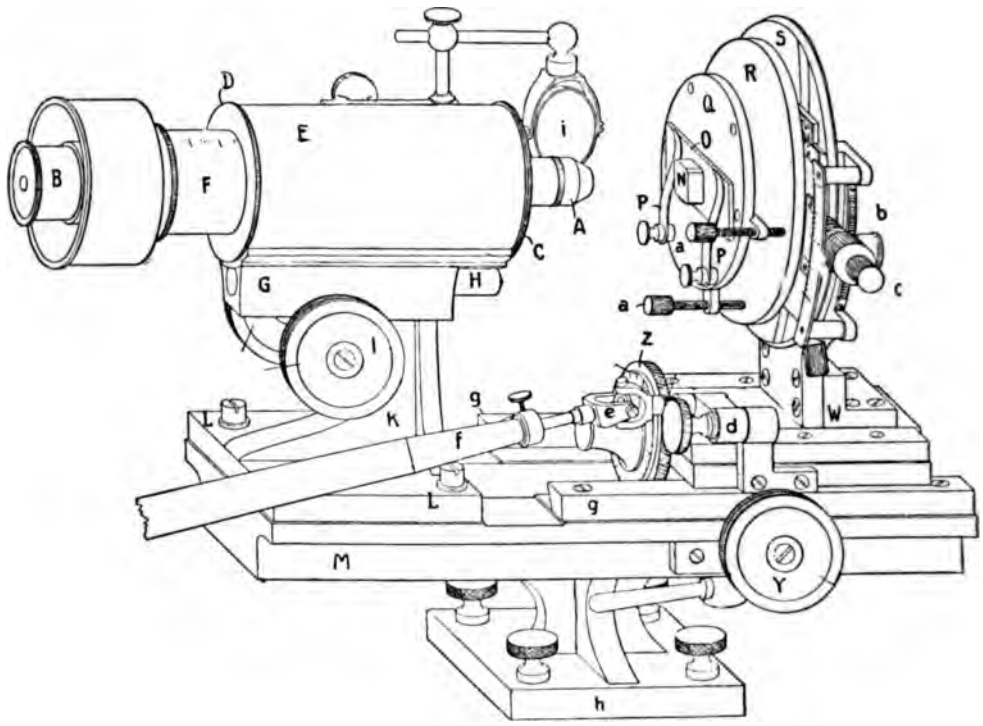

Fig. 31. — Martens metallurgical microscope.

adjustments, and all controlling heads are placed beneath. Appliances are provided for various kinds of illumination. The necessary alteration of focus for photographing can be done at the eye-piece by a suitable arrangement provided for that purpose.

Osmond. — Osmond used a Nachet microscope of the ordinary type connected with a vertical camera and a prism illuminator. He writes, however, that special metallurgical microscopes "are certainly to be preferred." In Osmond's opinion the vertical is very much superior to the horizontal camera for studying metals.

Nachet. — Nachet of Paris constructs the metallurgical microscope (Fig. 35). The vertical illuminator carries a tube provided with an iris diaphragm. The stand is to be used in the vertical position only. The stage has a coarse vertical adjustment. A similar microscope is made with mechanical stage provided with both coarse and fine adjustments.

The prism illuminator (Fig. 36) designed by Guillemin is made by Nachet. A

lateral as well as a slight tilting motion may be imparted to the prism through the milled heads *B* and *C*.

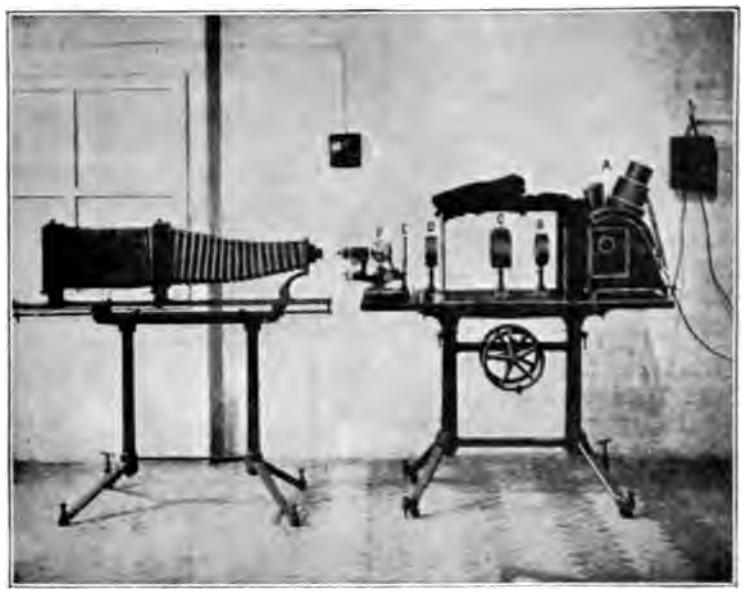

Fig. 32. — Martens-Zeiss metallurgical microscope and camera.

Fig. 33. — Martens ball-jointed microscope.

Nachet's illuminating objectives have been described and illustrated (Apparatus for the Metallographic Laboratory, page 17).

Cornu-Charpy. — The arrangement shown in Figure 37 was used by Charpy. The vertical illuminator *G* consists of four thin glass plates placed at an angle of 45 deg.

immediately below the eye-piece and it receives the light reflected by the totally reflecting prism *P*. This prism is so mounted that it can rotate freely around the axis of the microscope and also around the axis *GP* of the tube to which it is attached, thus making it possible to receive upon it the light proceeding from a source of light placed anywhere.

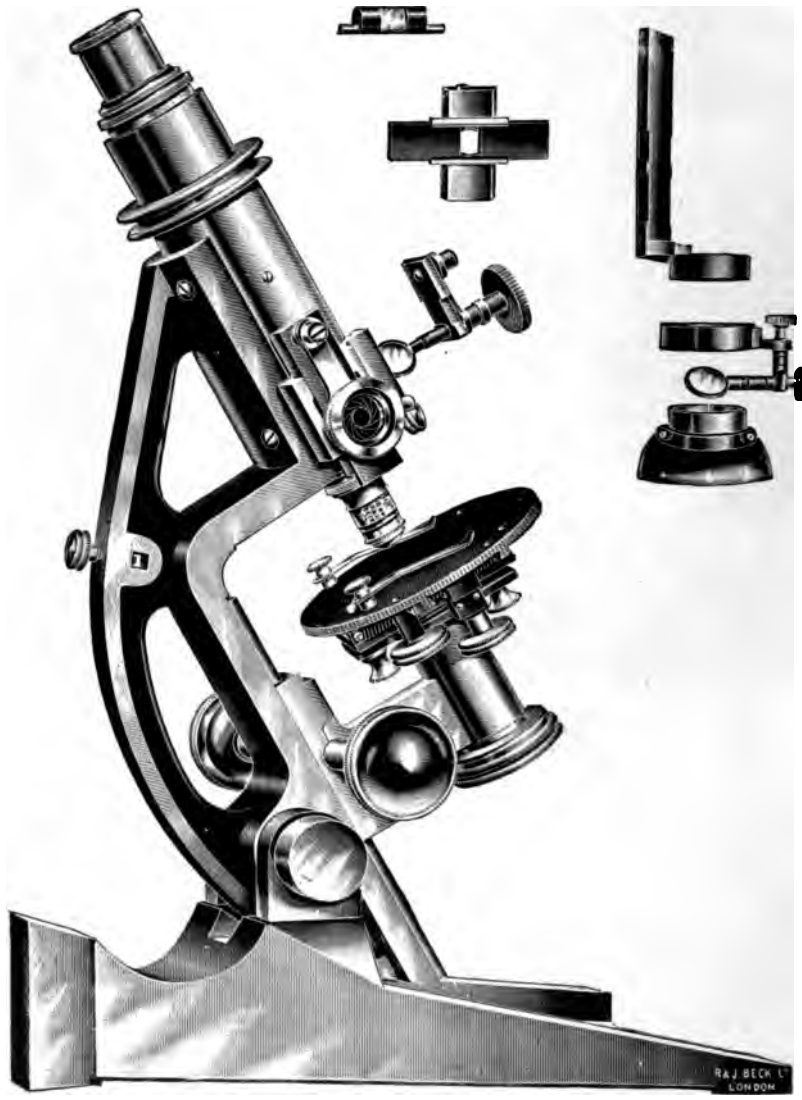

Fig. 34. — Rosenhain metallurgical microscope.

Watson and Sons. — The metallurgical microscope (Fig. 38) was constructed in 1904 by Watson and Sons of London. The stage is provided with both coarse and fine adjustments. The same makers following Martens construct the horizontal metallurgical microscope (Fig. 39). The plain glass vertical illuminator (Fig. 40) provided with iris diaphragm is also made by Watson and Sons.

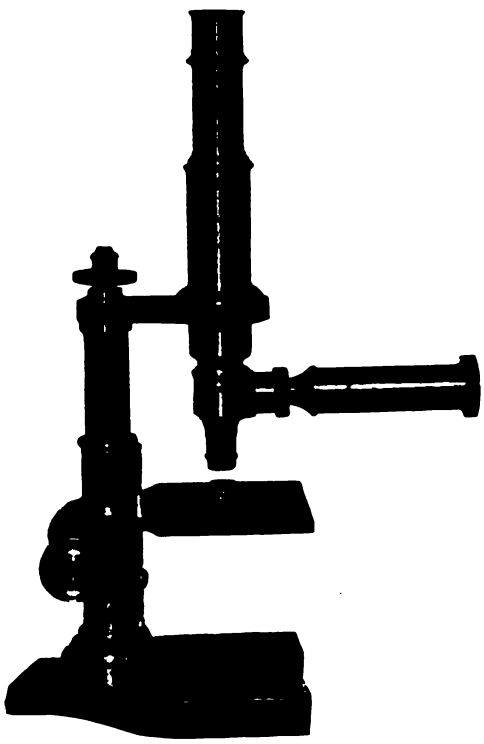

Fig. 35. — Nachet metallurgical microscope.

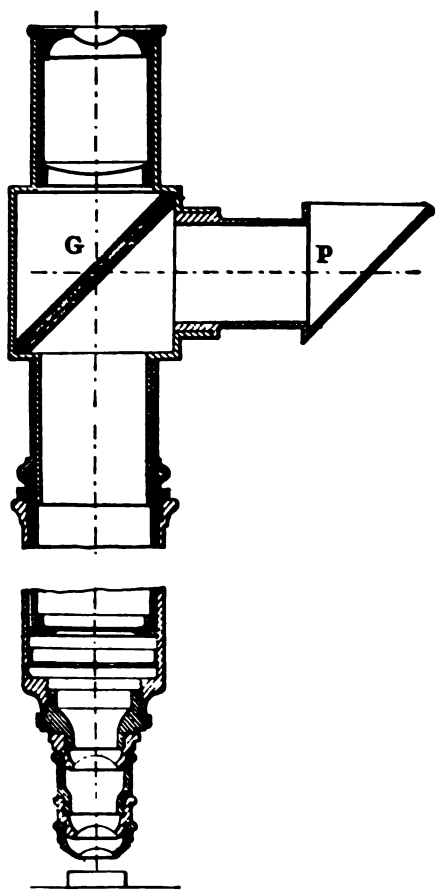

Fig. 37. — Cornu-Charpy metallurgical microscope.

Fig. 36. — Guillemin-Nachet prism illuminator.

Fig. 38. — Metallurgical microscope constructed by Watson and Sons.

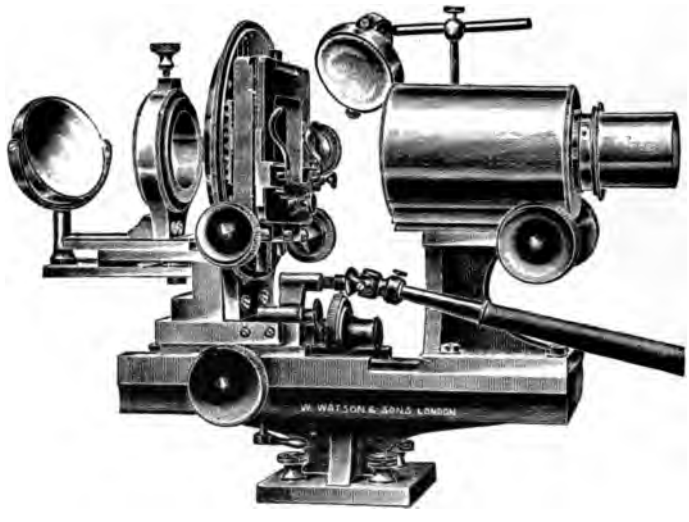

Fig. 39. — Horizontal metallurgical microscope constructed by Watson and Sons.

R. and J. Beck. — In 1904 R. and J. Beck of London constructed the prism vertical illuminator shown in Figure 41. The device is fitted with an iris diaphragm

Fig. 40. — Watson and Sons vertical illuminator.

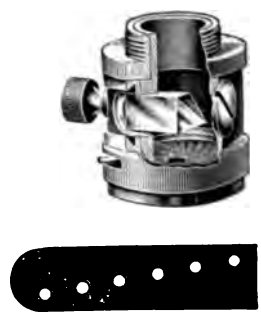

Fig. 41. — Beck prism illuminator.

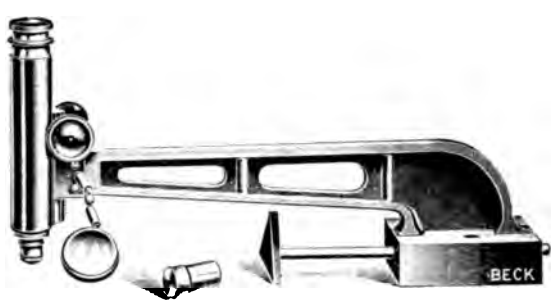

Fig. 42. — Beck surface microscope.

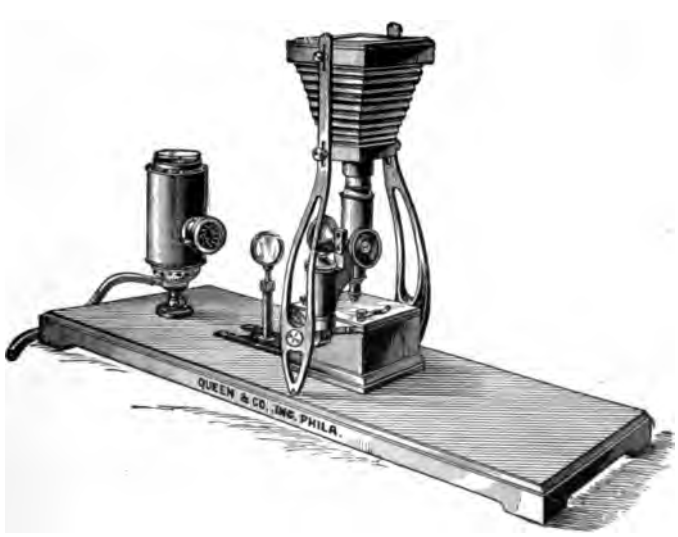

Fig. 43. — Metallurgical microscope. (Queen and Co.)

beneath the prism for cutting off outside light, and a plate of stops so arranged that the position of the beam of light impinging on the prism can be varied until parallel light of the right angle is obtained. The same makers construct the instrument

shown in Figure 42 for the examination of large metallic surfaces. The Rosenhain microscope described in these pages is likewise made by R. and J. Beck.

Queen and Co. — Queen and Co. of Philadelphia at one time (1898) placed on the market the microscope and camera shown in Figure 43. The camera could be tilted on one side for ocular examination. The same makers now construct the microscope shown in Figure 44.

Arthur H. Thomas Co. — Arthur H. Thomas Co. of Philadelphia are offering

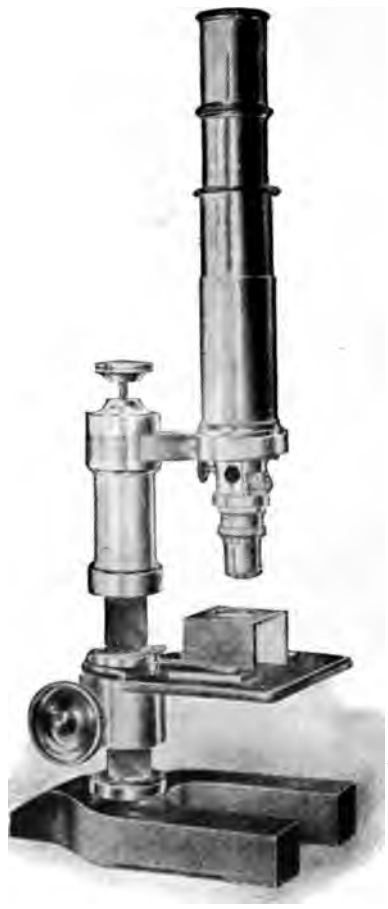

Fig. 44. — Metallurgical microscope. (Queen and Co.)

for sale an illuminator designed by Wirt Tassin (Fig. 45). A condensing lens and acetylene burner are attached to the vertical illuminator.

F. Koristka. — The prism vertical illuminator (Fig. 46) was described by F. Koristka of Milan in 1905. An iris diaphragm placed in front of the prism controls the light which it receives. By pulling out the arm carrying the prism the latter may be removed from the field.

Ph. Pellin. — The Le Chatelier inverted microscope is constructed by Ph. Pellin of Paris. The same makers also manufacture a portable microscopic outfit designed

by Guillet (*Trousse de Métallographie*). It includes a small electric motor for polishing, a vertical microscope so constructed that it can be fastened to any object it is

Fig. 45. — Microscope and camera with Tassin illuminator attached.

Fig. 46. — Koristka prism illuminator.

desired to examine, files, emery-papers, etching reagents, etc. All parts are compactly placed in a carrying case.

Carl Zeiss. — The instruments used by Martens and Heyn already described in these pages are constructed by Carl Zeiss of Jena. The prism vertical illuminator made by the same firm has been described and illustrated in the introductory chapter on Apparatus.

Spencer Lens Co. — The Spencer Lens Co. of Buffalo, N. Y., manufacture a vertical metallurgical microscope with movable stage.

Bausch and Lomb Optical Co. — The microscopes and accessories used and designed by the author and fully described in these pages are manufactured by the Bausch and Lomb Optical Co. of Rochester, N. Y.

APPENDIX II

REPORT OF COMMITTEE 53 OF THE INTERNATIONAL ASSOCIATION FOR TESTING MATERIALS

ON THE NOMENCLATURE OF THE MICROSCOPIC SUBSTANCES AND STRUCTURES OF STEEL AND CAST IRON

Presented by the Chairman H. M. Howe and the Secretary of the Committee Albert Sauveur at the VIth Congress, New York, September, 1912

The Committee for studying this problem is constituted as follows:

Professor H. M. Howe, Chairman, New York.

Professor Albert Sauveur, Secretary, Cambridge, Mass.

Members: F. Osmond, Paris; Dr. H. C. H. Carpenter, Manchester; Prof. W. Campbell, New York; Prof. C. Benedicks, Stockholm; Prof. F. Wüst, Aachen; Prof. A. Stansfield, Montreal; Dr. J. E. Stead, Middlesbrough; Prof. L. Guillet, Paris; Prof. E. Heyn, Berlin-Lichterfelde; Dr. W. Rosenhain, Teddington.

I. GENERAL PLAN

We first enumerate the substances of such importance as to warrant it, indicating roughly their constitution, and then define and describe certain of them.

The conditions which we meet are (1) that we need definitions on which all can agree; and this implies that they must be free from all contentious matter and be based on what all admit to be true; (2) that the reader must needs know the current theories as to the constitution of these substances, and these theories are necessarily contentious. We meet these conditions by the plan of giving (1) the *Name* which we recommend for general use, followed immediately in parentheses by the other names used widely enough to justify recording them; (2) the *Definition* proper, based on an undisputed quality, e.g. that of austenite, which we base on its being an iron-carbon solid solution, purposely omitting all reference to the precise nature of solvent and solute; and (3) *Constitution*, etc., etc., in which we give the current theories as to the nature of solvent and solute and appropriate descriptive matter.

The distinction between these three parts should be understood. (1) The *Names* actually used are matters of record and indisputable. (2) The *Definitions* are matters of convention or treaty, binding on the contracting parties, though subject to denouncement, preferably based on some determinable property of the thing defined as distinguished from any theory as to its nature, or if necessarily based on any theory it should be a theory which is universally accepted. It is a matter purely of convention and general convenience what individual property of the thing defined shall form the basis of the definition. The name and the definition should endure permanently, except in the case of a definition based on an accepted theory, which must be

changed if the theory should later be disproved. (3) *Theories* and *Descriptions* are not matters of agreement or convention but dependent on observation, and therefore always subject to be changed by new discoveries. They are temporary in their nature as distinguished from the names and definitions which should be fixed, at least relatively.

This case of austenite illustrates the advantage of non-indicative names. The names which we propose to displace, "gamma iron" and "mixed crystals," imply definite theories as to the nature of austenite, and hence might have to be abandoned in case those theories were later disproved. The name "austenite" implies nothing, like mineralogical names in general, and hence is stable in itself. Our infant branch of science may well learn from its elder sister, which has tried and proved the advantage of this non-indicative naming.

In those cases in which a name has been used in more than one sense we advise the retention of one and the abandonment of the others, having obtained the consent of the proposers of such names for their abandonment.

Many whose judgment we respect object to our including certain of the less used names, e.g. from *i* to *n* in our list, holding them either to be confusing or to be needless.

It is true that several names (hardenite, martensite, sorbite, etc.), have been used with various meanings, and hence confusingly, in spite of which most of them should be retained, each with a single sharp-cut definition, because they are so useful.

As regards the alleged needlessness of certain names it is for each writer to decide whether he does or does not need names with nice shades of meaning, such as osmondite and troosto-sorbite. Those who look only at the general outlines and not at the details have no right to forbid the workers in detail from having and using words fitting their work; nor have those whose needs are satisfied by the three primary colors a right to forbid painters, dyers, weavers, and others from naming the many shades with which they are concerned. Like the lexicographer we must serve the reader by explaining those words which he will meet, whether we individually use or condemn them. We feel that we have exhausted our powers in cautioning writers that certain words are rare and not likely to be understood by most readers, or are improper for any reason, and in urging the complete abandonment of those withdrawn by their proposers.

Needless words will die a natural death; needed ones we cannot kill. The good we might do in hastening the death of the moribund by omitting them from this report is less than the good we do by teaching their meaning to those who will meet them in ante-mortem print. These readers have rights. We serve no class, but the whole.

Illustrations. — At the end of the several descriptions the reader is referred to good illustrations in Osmond and Stead's "Microscopic Analysis of Metals," Griffin & Co., London, 1904.

II. LIST OF MICROSCOPIC SUBSTANCES

The microscopic substances here described consist of

1. *Metarals*, true phases, like the minerals of nature. These are either elements, definite chemical compounds, or solid solutions and hence consisting of definite substances in varying proportions. These include austenite, ferrite, cementite, and graphite.

2. *Aggregates*, like the petrographic entities as distinguished from the true minerals. These mixtures may be in definite proportions, i.e. eutectic, or eutectoid mixtures (ledeburite, pearlite, steadite), or in indefinite proportions (troostite, sorbite). Those aggregates which are important for any reason are here described.

(Many true minerals, such as mica, felspar, and hornblende, are divisible into several different species so that these true mineral names may be either generic or specific. These genera and species are definite chemical compounds in which one element may replace another. Other minerals, such as obsidian, are solid solutions in varying proportions, and in these also one element may replace another. Metarals like minerals differ from aggregates in being severally chemically homogeneous.)

These two classes may be cross classified into:

(*A*) The iron-carbon series, which come into being in cooling and heating.

(*B*) The important impurities, manganese sulphide, ferrous sulphide, slag, etc.

(*C*) Other substances.

The most prominent members of the iron-carbon series are:

I. molten iron, metaral, molten solution, but hardly a microscopic constituent;

II. the components which form in its solidification:

(*a*) austenite, solid solution of carbon or iron carbide in iron, metaral,

(*b*) cementite, definite metaral, Fe_3C,

(*c*) graphite, definite metaral, C;

III. the transition substances which form through the transformation of austenite during cooling:

(*d*) martensite, metaral of variable constitution; its nature is in dispute;

(*e*) troostite, indefinite aggregate, uncoagulated mixture,

(*f*) sorbite, indefinite aggregate, chiefly uncoagulated pearlite plus ferrite or cementite;

IV. products[1] of the transformation of austenite:

(*g*) ferrite,

(*h*) pearlite.

This transformation may also yield cementite and graphite as end products in addition to those under *b* and *c*.

In addition to the above, the names of which are universally recognized and in general use, the following names have been used more or less:

(*i*) ledeburite (Wüst), definite aggregate, the austenite-cementite eutectic;

(*j*) ferronite (Benedicks), hypothetical definite metaral, β iron containing about 0.27 per cent of carbon;

(*k*) steadite (Sauveur), definite aggregate, the iron-phosphorus eutectic (rare);

and three transition stages in the transformation of austenite, viz.:

(*l*) hardenite (Arnold), collective name for the austenite and martensite of eutectoid composition;

(*m*) osmondite (Heyn), boundary stage between troostite and sorbite;

(*n*) troosto-sorbite (Kourbatoff), indefinite aggregate, the troostite and the sorbite which lie near the boundary which separates these two aggregates (obsolescent).

[1] In hypo-eutectoid steels these habitually play the part of end products, though according to the belief of most the true end of the transformation is not reached till the whole has changed into a conglomerate of ferrite plus graphite.

III. DEFINITIONS AND DESCRIPTIONS

Carbon-iron Equilibrium Diagram, Figure 1. — Under the several substances abo to be described an indication will be given of the parts of the carbon-iron equilibriu diagram Figure 1 to which they severally correspond.

Austenite, Osmond (Fr. Austénite, Ger. Austenit, called also mixed crystals a gamma iron. Up to the year 1900 often called martensite and wrongly sometim still so called). Metaral of variable composition.

Definition. — The iron-carbon solid solution as it exists above the transformatio

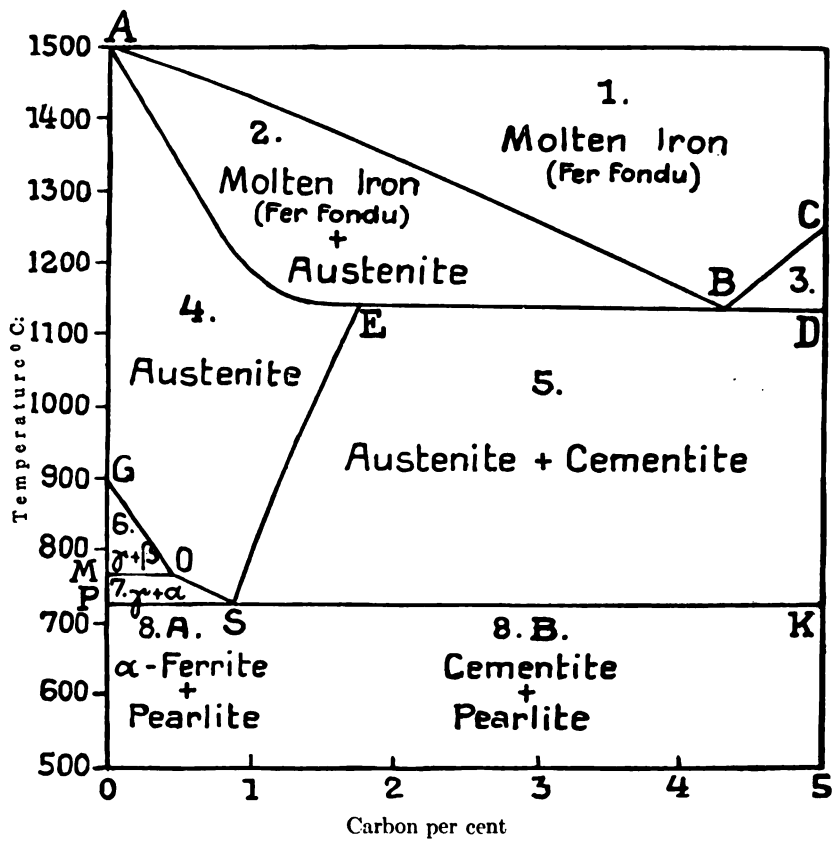

Fig. 1. — A_1: The line PSK is often called "A_1". A_3: The line GOS is often called "A_3", and this name is sometimes applied to the line SE.

range or as preserved with but moderate transformation at lower temperatures, e.g. by rapid cooling, or by the presence of retarding elements (Mn, Ni, etc.), as in 12 per cent manganese steel and 25 per cent nickel steel.

Constitution and Composition. — A solid solution of carbon or iron carbide (probably Fe_3C) and gamma iron, normally stable only above the line PSK of the carbon-iron diagram. It may have any carbon content up to saturation as shown by the line SE, viz.: about 0.90 per cent at S (about 725 deg. C.) to 1.7 per cent at E (about 1130 deg.). The theory that the iron and the carbide of carbon, instead of being dissolved in each other, are dissolved in a third substance, the solution of eutectoid com-

position ($Fe_{24}C$, called hardenite) is not in accord with the generally accepted theory of the constitution of solutions, and is not entertained widely or by any member of this committee.

Crystallization. — Isometric. The idiomorphic vug crystals are octahedra much elongated by parallel growth. The etched sections show much twinning. (Osmond and most authorities.) Le Chatelier believes it to be rhombohedral. Cleavage octahedral.

Varieties and Genesis. — (1) Primary austenite formed in the solidification of carbon steel and hypo-eutectic cast iron; (2) eutectic austenite, interstratified with eutectic cementite, making up the eutectic formed at the end of the solidification of steel containing more than about 1.7 per cent of carbon, and of all cast iron.

Equilibrium. — It is normal and in equilibrium in Region 4, and also associated with beta iron in Region 6, with *a* iron in Region 7, and with cementite in Region 5. It should normally transform into pearlite with either ferrite or cementite on cooling past A_1 into Region 8.

Transformation. — In cooling slowly through the transformation range, $Ar_3 - Ar_1$, austenite shifts its carbon content spontaneously through generating pro-eutectoid ferrite or cementite, to the eutectoid ratio, about 0.90 per cent, and then transforms with increase of volume at Ar_1 into pearlite, q.v., with which the ejected ferrite or cementite remains mixed. Rapid cooling and the presence of carbon, manganese, and nickel obstruct this transformation, (1) retarding it, and (2) lowering the temperature at which it actually *occurs*, and in addition (3) manganese and nickel lower the temperature at which in equilibrium it is *due*. Hence, by combining these four obstructing agents in proper proportions the transformation may be arrested at any of the intermediate stages, martensite, troostite, or sorbite,[1] q.v., and if arrested in an earlier stage it can be brought to any later desired stage by a regulated reheating or "tempering." For instance, though a very rapid cooling in the absence of the three obstructing elements checks the transformation but little and only temporarily, yet if aided by the presence of a little carbon it arrests the transformation wholly in the martensite stage; and in the presence of about 1.50 per cent of carbon such cooling retains about half the austenite so little altered that it is "considerably" softer than the usually darker needles of the surrounding martensite, with which it contrasts sharply. Again, either (*a*) about 12 per cent of manganese plus 1 per cent of carbon, or (*b*) 25 per cent of nickel, lower and obstruct the transformation to such a degree that austenite persists in the cold apparently unaltered, even through a slow cooling. (Hadfield's manganese steel and 25 per cent nickel steel, manganiferous and nickeliferous austenite respectively.)

Occurrence. — When alone (12 per cent manganese and 25 per cent nickel steel and Maurer's 2 per cent carbon plus 2 per cent manganese austenite) polyhedra, often coarse, much twinned at least in the presence of martensite, and readily developing slip bands. In hardened high-carbon steel it forms a ground mass pierced by zigzag needles and lances of martensite.

Etching. — All the common reagents darken it much more than cementite, less

[1] Though the transformation can be arrested in such a way as to leave the whole of the steel in the condition of martensite, it is doubted by some whether it can be so arrested as to leave the whole of it in any of the other transition stages. Troostite and sorbite caused by such arrest are habitually mixed, troostite with martensite or sorbite or both, and sorbite with pearlite or troostite or both.

than troostite or sorbite, and usually less, though sometimes more, than martensite, which is recognized by its zigzag shape and needle structure. With ferrite and pearlite it is never associated.

Physical Properties. — Maurer's austenite of 2 per cent manganese plus 2 per cent carbon is but little harder than soft iron, and 25 per cent nickel steel and Hadfield's manganese steel are but moderately hard. Yet as usually preserved in hardened high carbon steel, the hardness of austenite does not fall very far short of that of the accompanying martensite, probably because partly transformed in cooling. (Osmond's words are that it is "considerably" softer than that martensite.)

Specific Magnetism. — Very slight unless perhaps in intense fields. In Hadfield's manganese steel and 25 per cent nickel steel, very ductile.

Illustrations. — "Microscopic Analysis of Metals," Figures 20, 50, and 51 on pp. 39, 100, and 101.

Cementite (Sorby, "intensely hard compound"; Ger. Cementit, Fr. Cémentite; Arnold, crystallized normal carbide). Definite metaral.

Definition. — Tri-ferrous carbide, Fe_3C. The name is extended by some writers so as to include tri-carbides in which part of the iron is replaced by manganese or other elements. Such carbides may be called "manganiferous cementite," etc.

Occurrence. — (*a*) Pearlitic as a component of pearlite, q.v.; (*b*) eutectic; (*c*) primary or pro-eutectic; (*d*) pro-eutectoid; (*e*) that liberated by the splitting up of the eutectic or of pearlite; and (*f*) uncoagulated in sorbite, troosite, and perhaps martensite. (*c*), (*d*), and (*e*) are grouped together as "free" or "massive."

Primary cementite is generated in cooling through Region 3; eutectic cementite on cooling past the line EBD; pro-eutectoid cementite in cooling through Region 5; pearlitic cementite on cooling past the line PSK, or A_1. Though the several varieties of cementite are generally held to be all metastable, tending to break up into graphite plus either austenite above A_1 or ferrite below A_1, yet they have a considerable and often great degree of persistence. The graphitizing tendency is completely checked in the cold but increases with the temperature and with the proportion of carbon and of silicon present, and is opposed by the presence of manganese.

Crystallization. — Orthorhombic, in plates.

Structure. — (*a*) Pearlitic, in parallel unintersecting plates alternating with plates of ferrite; (*b*) eutectic, plates forming a network filled with a fine conglomerate of pearlite with or without pro-eutectoid cementite; (*c*) primary, in manganiferous white cast iron, etc., in rhombohedral plates; (*d*) in hyper-eutectoid steel, pro-eutectoid cementite forms primarily a network enclosing meshes of pearlite through which cementite plates or spines sometimes shoot if the network is coarse; (*e*) cementite liberated from pearlite merges with any neighboring cementite; (*f*) the structure of uncoagulated cementite cannot be made out. On long heating the pro-eutectoid and pearlitic cementite spheroidize slowly, and neighboring particles merge; (*g*) in white irons rich in phosphorus in flat plates embedded in iron-carbon-phosphorus eutectic.

Etching, etc. — After polishing stands in relief. Brilliant white after etching with dilute hydrochloric or picric acid; darkened by boiling with solution of sodium picrate in excess of sodium hydrate.

Physical Properties. — Hardest component of steel. Hardness = 6 of Mohs scale. Scratches glass and felspar but not quartz; very brittle. Specific magnetism about two thirds that of pure iron.

Illustrations. — "Microscopic Analysis of Metals," Figures 42 and 43 on pp. 84, 85.

Martensite (Fr. Martensite, Ger. Martensit). Metaral. Its nature is in dispute.

Definition. — The early stage in the transformation of austenite characterized by needle structure and great hardness, as in hardened high-carbon steel.

Constitution. — I. (Osmond and others.) A solid solution like austenite, q.v., except that the iron is partly beta, whence its hardness, and partly alpha, whence its magnetism in mild fields. II. (Le Chatelier.) The same except that its iron is essentially alpha, and the hardness due to the state of solid solution. III. (Arnold.) A special structural condition of his "hardenite" (austenite); not widely held. IV. A solid solution in gamma iron. V. (Benedicks.) The same as I, except that the iron is wholly beta and that beta iron consists of alpha iron containing a definite quantity of gamma iron in solution.

Equilibrium. — It is not in equilibrium in any part of the diagram, but represents a metastable condition in which the metal is caught during rapid cooling, in transit between the austenite condition stable above the line A_1 and the condition of ferrite plus cementite into which the steel habitually passes on cooling slowly past the line A_1.

Occurrence. — The chief constituent of hardened carbon tool steels, and of medium nickel and manganese steels. In still less fully transformed steels (1.50 per cent carbon steel rapidly quenched, etc.) it is associated with austenite; in more fully transformed ones (lower carbon steels hardened, high carbon steels oil hardened, or water hardened and slightly tempered, or hardened thick pieces even of high carbon steel) it is associated with troostite, and with some pro-eutectoid ferrite or cementite, q.v., in hypo- and hyper-eutectoid steels respectively. In tempering it first changes into troostite; at 350 deg. – 400 deg. it passes through the stage of osmondite; at higher temperatures it changes into sorbite; and at 700 deg. into granular pearlite. On heating into the transformation range this changes into austenite, which on cooling again yields lamellar pearlite.

Characteristic specimens are had by quenching bars 1 cm. square of eutectoid steel, i.e. steel containing about 0.9 per cent of carbon, in cold water from 800 deg. C. (1472 deg. F.).

Structure. — When alone, habitually in flat plates made up of intersecting needles parallel to the sides of a triangle. When mixed with austenite, zigzag needles, lances, and shafts.

If produced by quenching after heating to 735 deg. C., it consists of minute crystallites resembling the globulites of Vogelsang, which are rarely arranged in triangular order. At times so fine as to suggest being amorphous.

Etching. — With picric acid, iodine or very dilute nitric acid etches usually darker than austenite, but sometimes lighter, always darker than ferrite and cementite, but always lighter than troostite.

Illustrations. — "Microscopic Analysis of Metals," Figure 19 on p. 38, Figure 52 on p. 102.

Ferrite (Fr. Ferrite, Ger. Ferrit). Definite metaral.

Definition. — Free alpha iron.

Composition. — Nearly pure iron. It may contain a little phosphorus and silicon but its carbon content, if any, is always small, at the most not more than 0.05 per cent, and perhaps never as much as 0.02 per cent.

Occurrence. — (*a*) *Pearlitic* as a component of pearlite, q.v.; (*b*) pro-eutectoid ferrite generated in slow cooling through the transformation range; (*c*) that segregated from pearlite, i.e. set free by the splitting up of pearlite, especially in low carbon steel; (*d*) *uncoagulated* as in sorbite, and probably troostite. (*b*) and (*c*) are classed together as free or massive.

Thus ferrite is normal and stable in regions 7 and 8.

Crystallization. — Isometric, in cubes or octahedra.

Structure. — (*a*) Pearlitic ferrite, unintersecting parallel plates alternating with plates of cementite; (*b*) pro-eutectoid ferrite in low carbon steel forms irregular polygons, each with uniform internal orientation. In higher carbon steel after moderately slow cooling, especially in the presence of manganese, it forms a network enclosing meshes of pearlite. In slower cooling this network is replaced by irregular grains separated by pearlite; (*c*) the ferrite set free by the splitting up of pearlite merges with the pro-eutectoid ferrite, if any; (*d*) the structure of the ferrite in sorbite, etc., cannot be made out.

Etching. — Dilute alcoholic nitric or picric acid on light etching leaves the ferrite grains white with junctions which look dark. Deeper etching, by Heyn's reagent or its equivalent, reveals the different orientation of the crystals or grains, (*a*) as square figures parallel to the direction of the etched surface, (*b*) as plates which dip at varying angles and become dark or bright when the specimen is rotated under oblique illumination. Still deeper etching reveals the component cubes (etching figures, Ätzfiguren), at least if the surface is nearly parallel to the cube faces.

Physical Properties. — Soft; relatively weak (tenacity about 40,000 lbs., per sq. in.); very ductile; strongly ferro-magnetic; coercitive force very small.

Grain Size. — For important purposes (1) etch deeply enough, e.g. with copper-ammonium chloride, to reveal clearly the junctions of the grains; (2) count on a photograph of small magnification the number of grains in a measured field so drawn as to exclude fragments of grains; after (3) determining the true grain boundaries by examination under high powers (Heyn's method). Deep nitric acid etching is inaccurate, because an apparent grain boundary may contain several grains.

Illustrations. — "Microscopic Analysis of Metals," Figures 41, 56 on pp. 79, 116.

Osmondite (Fr. Osmondite, Ger. Osmondit).

Definition. — That stage in the transformation of austenite at which the solubility in dilute sulphuric acid reaches its maximum rapidity. Arbitrarily taken as the boundary between troostite and sorbite.

Earlier Definition. — Defined by the Vth Congress as having the "maximum solubility in acids and by a maximum coloration under the action of acid metallographic reagents." The present definition is confined to maximum rapidity of dissolving, because we do not yet know that this in all cases co-exists with the maximum depth of coloration, and in any case in which these two should not co-exist, the old definition does not decide which is true osmondite.

Constitution. — The following hypotheses have been suggested, none of which has firm experimental foundation: (1) A solid solution of carbon or an iron carbide in alpha iron. (2) The colloidal system of Benedicks in its purity, troostite being this system while forming at the expense of martensite, and sorbite, being this system coagulating and passing into pearlite. (3) The stage of maximum purity of amorphous alpha iron on the way to crystallizing into ferrite.

Occurrence. — Hardened carbon steel of about 1 per cent of carbon when reheated

(tempered) to 350–400 deg. C. passes through the stage of troostite to that of osmondite, and on higher heating to that of sorbite. What variation if any from this temperature is needed to bring hardened steel of other carbon content to the osmondite stage is not known. In that it represents a true boundary state between troostite and sorbite it differs in meaning from troosto-sorbite, which embraces both the troostite and the sorbite which lie near this boundary. Indeed osmondite has sometimes been used in this looser sense. Writers are cautioned that, however useful these terms may prove for making these nice discriminations, they are not likely to be familiar to general readers.

Etching. — According to Heyn it differs from troostite and sorbite in being that stage in tempering which colors darkest on etching with alcoholic hydrochloric acid.

The present definition and description of osmondite should displace previous ones, because they have the express approval of Professor Heyn, the proposer of the name, and M. Osmond himself.

Ferronite (Fr. Ferronite, Ger. Ferronit) (Benedicks). Hypothetical definite metaral.

Definition. — Solid solution of about 0.27 per cent of carbon in beta iron.

Occurrence (hypothetical). — In slowly cooled steels and cast iron containing 0.50 per cent of combined carbon or more, that which is generally believed to be ferrite, whether pearlitic or free, is supposed by Benedicks to be ferronite.

Hardenite (Fr. Hardenite, Ger. Hardenit).

Definition. — Collective name for austenite and martensite of eutectoid composition. It includes such steel (1) when above the transformation range, and (2) when hardened by rapid cooling.

Observations. — On the generally accepted theory that austenite is a solid solution of carbon or an iron carbide in iron, hardenite is the solution of the lowest transformation temperature, i.e. the eutectoid. The theory that instead it is a definite chemical compound, $Fe_{24}C$, is considered under Austenite. Its proposer includes under hardenite both eutectoid (0.90 per cent carbon) austenite when above the transformation range and the martensite into which that austenite shifts in rapid cooling (hardening).

Other Meanings. — Originally (Howe, 1888) collective name for austenite and martensite of any composition in carbon steel. Osmond (1897), austenite saturated with carbon. Both these meanings are withdrawn by their proposers.

Pearlite (Sorby's "pearly constituent." At first written "pearlyte" Fr. Perlite, Ger. Perlit). Aggregate.

Definition. — The iron-carbon eutectoid, consisting of alternate masses of ferrite and cementite.

Constitution and Composition. — A conglomerate of about 6 parts of ferrite to 1 of cementite. When pure, contains about 0.90 per cent of carbon, 99.10 per cent of iron.

Occurrence. — Results from the completion of the transformation of austenite brought spontaneously to the eutectoid carbon content, and hence occurs in all carbon steels and cast iron containing combined carbon and cooled slowly through the transformation range, or held at temperatures in or but slightly below that range, long enough to enable the ferrite and cementite to coagulate into a mass microscopically resoluble. Hence it is the normal constituent in Region 8. Its ferrite is stable but its cementite is metastable and tends to transform into ferrite and graphite.

Varieties and Structure. — Because pearlite is formed by the coagulation of the

ferrite and cementite initially formed as the irresoluble emulsion, sorbite, (Arnold's sorbitic pearlite) there are the indefinitely bounded stages of *sorbitic pearlite* (Arnold's normal pearlite), i.e. barely resoluble pearlite, in the border-land between sorbite and laminated pearlite; *granular pearlite*, in which the cementite forms fine globules in a matrix of ferrite; and *laminated* or *lamellar pearlite*, consisting of fine, clearly defined, non-intersecting, parallel lamellæ alternately of ferrite and cementite. The name *granular pearlite* was first used by Sauveur to represent what is now called sorbite. This meaning has been withdrawn.

An objection to Arnold's name "normal pearlite" is that it is likely to mislead. "Normal" here apparently refers to arising under normal conditions of cooling, but (1) it rather suggests structure normal for pearlite, which surely is the lamination characteristic of eutectics in general, and (2) the general reader has no clue as to what conditions of cooling are here called normal. Many readers are not manufacturers, and even in manufacture itself air cooling is normal for one branch and extremely slow furnace cooling for another. Arnold calls troostite "troostitic pearlite" and sorbite "sorbitic pearlite." This is contrary to general usage, which restricts pearlite to microscopically resoluble masses.

Etching. — After etching with dilute alcoholic nitric or picric acid it is darker than ferrite or cementite but lighter than sorbite and troostite. A magnification of at least 250 diameters is usually needed for resolving it into its lamellæ, though the pearlite of blister steel can often be resolved with a magnification of 25 diameters. The more rapidly pearlite is formed, the higher the magnification needed for resolving it.

Illustrations. — Lamellar pearlite. Osmond and Stead, "Microscopic Analysis," Figure 11 on p. 19, Granular pearlite, *idem*, Figure 18 on p. 36; Heyn and Bauer, "Stahl und Eisen," 1906, Figure 14, opposite p. 785.

Graphite (Ger. Graphit, Fr. Graphite). Definite metaral.

Definition. — The free elemental carbon which occurs in iron and steel.

Composition. — Probably pure carbon, identical with native graphite.

Genesis. — Derived in large part, and according to Gœrens wholly, from the decomposition of solid cementite. Others hold that its formation as kish may be from solution in the molten metal, and that part of the formation of temper graphite may be from elemental carbon dissolved in austenite. It is the stable form of carbon in all parts of the diagram.

Occurrence. — (1) as kish, flakes which rise to the surface of molten cast iron and usually escape thence;

(2) as thin plates, usually curved, e.g. in gray cast iron, representing carbon which has separated during great mobility, i.e. near the melting range;

(3) as temper graphite (Ger. Temperkohle, Ledebur) pulverulent carbon which separates from cementite and austenite, especially in the annealing process for making malleablized castings.

Graphite and ferrite are sometimes associated in a way which suggests strongly that they represent a graphite-austenite eutectic. But the existence of such a true eutectic is doubted by most writers.

Properties. — Hexagonal. H. 1–2. Gr. 2.255. Streak black and shining, luster metallic; macroscopic color, iron black to dark steel gray, but always black when seen in polished sections of iron or steel under the microscope; opaque; sectile; soils paper; flexible; feel, greasy.

Troostite (Fr. Troostite, Ger. Troostit). Probably agrregate. (Arnold, troostitic pearlite.)

Definition. — In the transformation of austenite, the stage following martensite and preceding sorbite (and osmondite if this stage is recognized).

Constitution and Composition. — An uncoagulated conglomerate of the transition stages. The degree of completeness of the transformation represented by it is not definitely known and probably varies widely. Osmond and most others believe that the transformation, while generally far advanced, yet falls materially short of completion; but Benedicks and Arnold (9) believe that it is complete. The former belief that it is a definite phase, e.g. a solid solution of carbon or an iron carbide in either β or γ iron, is abandoned. Its carbon content like that of austenite and martensite varies widely.

Occurrence. — It arises either on reheating hardened (e.g. martensitic steel) to slightly below 400 deg., or on cooling through the transformation range at an intermediate rate, e.g. in small pieces of steel when quenched in oil, or quenched in water from the middle of the transformation range, or in the middle of larger pieces quenched in water from above the transformation range. With slightly farther reheating it changes into sorbite; with higher heating into sorbitic pearlite, then slowly into granular pearlite, and probably indirectly into lamellar pearlite. It occurs in irregular, fine-granular or almost amorphous areas, colored darker by the common etching reagents than the martensite or sorbite accompanying it. A further common means of distinguishing it from sorbite is that it is habitually associated with martensite, whereas sorbite is habitually associated with pearlite.

Areas near the boundary between troostite and sorbite are sometimes called troosto-sorbite.

Properties. — Hardness, intermediate between that of the martensitic and the pearlitic state corresponding to the carbon content of the specimen. In general the hardness increases, the elastic limit rises, and the ductility decreases, as the carbon content increases. Its ductility is increased rapidly and its hardness and elastic limit lowered rapidly by further tempering, which affects it much more markedly than sorbite.

Sorbite (Fr. Sorbite, Ger. Sorbit). Aggregate. (Arnold, sorbitic pearlite.)

Definition. — In the transformation of austenite, the stage following troostite and osmondite if the stage is recognized, and preceding pearlite.

Constitution and Composition. — Most writers believe that it is essentially an uncoagulated conglomerate of irresoluble pearlite with ferrite in hypo- and cementite in hyper-eutectoid steels respectively, but that it often contains some incompletely transformed matter.

Occurrence. — The transformation can be brought to the sorbitic stage (1) by reheating hardened steel to a little above 400 deg., but not to 700 deg. at which temperature it coagulates into granular pearlite; (2) by quenching small pieces of steel in oil or molten lead or even by air cooling them; (3) by quenching in water from just above the bottom of the transformation range, Ar_1. Sorbite is ill-defined, almost amorphous, and is colored lighter than troostite but darker than pearlite by the usual etching reagents. It differs further from troostite in being softer for given carbon content, and usually in being associated with pearlite instead of martensite, and from pearlite in being irresoluble into separate particles of ferrite and cementite.

As sorbite is essentially a mode of aggregation it cannot properly be represented

on the equilibrium diagram. Its components at all times tend to coagulate into pearlite, yet it remains in its uncoagulated state at all temperatures below 400 deg.

Properties. — Though slightly less ductile than pearlitic steel for given carbon content, its tenacity and elastic limit are so high that a higher combination of these three properties can be had in sorbitic than in pearlitic steels by selecting a carbon content slightly lower than would be used for a pearlitic steel. Hence the use of sorbitic steels, e.g. first hardened and then annealed cautiously, for structural purposes needing the best quality.

Manganese Sulphide (Fr. Sulphur de Manganèse, Ger. Schwefelmangan), MnS (Arnold and Waterhouse). Metaral.

Occurrence, etc. — Sulphur combines with the manganese present in preference to the iron, forming pale dove or slate gray masses, rounded in castings, elongated in forgings.

Ferrous Sulphide (Fr. Sulphure de Fer, Ger. Schwefeleisen), FeS. Metaral.

Occurrence. — The sulphur not taken up by the manganese forms ferrous sulphide, FeS, which, probably associated in part with iron as an Fe-FeS eutectic, forms by preference more or less continuous membranes surrounding the grains of pearlite. Color, yellow or pale brown.

Sulphur Prints. — When silk impregnated with mercuric chloride and hydrochloric acid (Heyn's and Bauer's method) or bromide paper moistened with sulphuric acid (Baumann's method) is pressed on polished steel, the position of the sulphur-bearing areas, whether of FeS or MnS, records itself by the local blackening which the evolved H_2S causes. Phosphorus bearing areas also blacken Baumann's bromide paper.

MISCELLANEOUS

Eutectoid, Saturated, etc. — The iron-carbon eutectoid is pearlite. Steel with more carbon than pearlite is called hyper-eutectoid, that with less is called hypo-eutectoid. Arnold's names "saturated," "unsaturated," and "supersaturated," for eutectoid, hypo-eutectoid, and hyper-eutectoid steel respectively, have considerable industrial use in English-speaking countries, but are avoided by most scientific writers on the ground that they are misleading, because, e.g. there is only one specific temperature, A_1, at which eutectoid steel is actually saturated, and, if any other temperature is in mind, that steel is not saturated. Above A_1 it is clearly undersaturated.

The objection to the names sorbite, troostite, martensite, and austenite, that each of them covers steel of a wide range of carbon content, is to be dismissed because a like objection applies with equal force to every generic name in existence.

The theoretical matter in this report is given solely for exposition and the committee disclaims the intent to impose any theory. This report is offered for adoption subject to this disclaimer on the ground that the adoption of theories is beyond the powers of a Congress.

INDEX

The Roman numerals refer to the numbers of the lessons, the letter A to the chapter on "Apparatus for the Metallographic Laboratory."

A

A, Ar, Ac, Ar_1, Ac_1, Ar_{1-2}, Ac_{1-2}, Ar_{1-2-3}, Ac_{1-2-3}, Ar_{cm}, Ac_{cm}. See critical points, notation
Allotrimorphic crystals, definition of, I, 2
Allotropic theory of the hardening of steel, XV, 2
Allotropy, definition of, II, 4
of cementite, VIII, 9
iron, II, 4; VIII, 1, 14
sulphur, II, 6
Alloy steels. See special steels
Alloys, constitution of, XXII, 1 to 21
, fusibility curves of, XXII, 5 to 21
, microstructure of, XXII, 5 to 21
of iron and carbon, equilibrium diagram of, XXIII, 12 to 21
, fusibility curves of, XXIII, 1 to 21
, phase rule applied to, XXIV, 6 to 8
, structural composition immediately after solidification of, XXIII, 3
, phase rule applied to, XXIV, 3 to 8
, solidification of, XXII, 3 to 21
, structural composition of, XXII, 15 to 20
whose component metals form solid solutions, solidification and constitution of, XXII, 3 to 9
are insoluble in each other in the solid state, solidification and constitution of, XXII, 9 to 17
partially soluble in each other in the solid state, solidification and constitution of, XXII, 17 to 21
Alpha iron, VIII, 1, 14; IX, 8
, crystallization of, II, 7
, description of, II, 6
theory of the hardening of steel, XV, 4
Alumina powder for polishing, preparation of, Appendix I, 2
Ammonium oxalate etching, V, 7
Anhedrons. See allotrimorphic crystals
Annealing, air cooling in, XII, 4
, cooling in, XII, 2
, double treatment in, XII, 8
for malleablizing cast iron, XXI, 3 to 7
, furnace cooling in, XII, 4
, heating for, XII, 1
, influence of maximum temperature in, XII, 5
, influence of time at maximum temperature in, XII, 6
, nature of operation, XII, 1

Annealing of steel, XII, 1 to 30
, oil and water quenching in, XII, 6
, purpose of, XII, 1
, rate of cooling vs. carbon content in, XII, 3
size of objects in, XII, 3
steel castings, XII, 13
temperatures for steel, XII, 2
Arnold on the hardening of steel, XV, 1, 4
Arnold's view of the nature of martensite, XIII, 10
troostite, XIII, 12
Austenite, crystallization of, X, 1 to 10
, definition, description, occurrence, and structure of, XIII, 3 to 9
, growth above the critical range of, XII, 20
, Osmond's test showing relative softness of, XIII, 7
, production by Maurer of, XIII, 5
Osmond of, XIII, 4
Robin of, XIII, 5
, relative softness of, XIII, 7
, saturated, XXIII, 2
Austenitic and pearlitic structures, relation between, XII, 21
special steels, XVII, 7
steel, tempering of, XIV, 3

B

Belaiew on the structure of steel and of meteorites, X, 6 to 10
Benedicks' equilibrium diagram of iron-carbon alloys, XXIII, 19
view of the nature of troostite, XIII, 12
Beta iron, VIII, 1, 11, 14; IX, 8
, crystallization of, II, 7
, description of, II, 6
theory of the hardening of steel, XV, 2
Binary alloys. See alloys.
Bivariant equilibrium, definition of, XXIV, 3
Black heart castings, XXI, 4
, annealing for, XXI, 5
Brass, twinnings in, II, 7
Brittleness, intercrystalline, XII, 27
, intergranular, XII, 27
of low carbon steel, XII, 26
Burnt steel, production and structure of, XII, 17 to 20

C

Cameras, A, 22 to 28
Carbide steel, XVII, 1
Carbon, condition of, in hardened and tempered steel, XIV, 8
, hardening and combined in steel, XIV, 8
in pearlite, V, 8
in steel, IV, 3
temper, XXI, 1
theory of the hardening of steel, XV, 1, 4
Carpenter and Keeling's cooling curves of steels, VII, 17
determinations of the critical points, VII, 8, 9
equilibrium diagram of iron-carbon alloys, XXIII, 18, 19
Case hardened articles, heat treatment of, XVI, 6
steel, tempering of, XVI, 6
hardening, composition of iron or steel subjected to, XVI, 1

Case hardening, cooling after, XVI, 5
, distribution of carbon after, XVI, 2
, duration of, XVI, 2
, materials used for, XVI, 3
, mechansim of, XVI, 5
of steel, XVI, 1 to 6
, temperatures for, XVI, 1
Cast iron, calculation of structural composition of, XIX, 5, 10 to 13; XX, 7 to 9
, chilled castings of, XIX, 13
, constitution, properties, and structure of, XIX, 1 to 13; XX, 1 to 10
containing only combined carbon, XIX, 3
graphitic carbon, XIX, 1
, formation of combined and graphitic carbon in, XIX, 1
, impurities in, XX, 1 to 10
, influence and occurrence of manganese in, XX, 2
phosphorus in, XX, 2
silicon in, XX, 1
sulphur in, XX, 1
, malleable, XXI, 1 to 8
, structural composition vs. physical properties of, XIX, 11
steel, structure of, X, 1 to 10
Castings suitable for malleablizing, XXI, 2
Cement carbon, definition of, XIV, 8
Cementation. See case hardening
of iron and steel, XVI, 1 to 6
Cementite, allotropy of, VIII, 9
, definition and description of, IV, 5
, etching of, V, 7; XIX, 4
, formation of, X, 4
, free, definition of, V, 5
, graphitizing of, XII, 15; XXI, 1; XXIII, 7
in high carbon steel, V, 4
, primary. See cementite, pro-eutectic
, pro-eutectic, XXIII, 5
, spheroidizing of, XII, 14
Cementitic special steels, XVII, 1, 8
Charpy and Grenet on the equilibrium diagram of iron-carbon alloys, XXIII, 20
on the hardening of steel, XV, 1, 5
Chilled castings, XIX, 13
Chrome-nickel steel, XVIII, 16
steel, XVIII, 13 to 15
, uses and properties of, XVIII, 14
-tungsten steel. See high-speed steel.
Chromium, influence on critical points of iron of, XVIII, 13
Cleavage, definition of, I, 1
brittleness. See intercrystalline brittleness, XII, 27
Cold working, crystalline growth after, I, 8
, influence on structure and properties of steel of, XI, 8
Colloidal solution, XIII, 12
Combined carbon in cast iron, XIX, 1, 3
Components, Bancroft's definition of, XXIV, 3
, definition of, XXIV, 3
, Findlay's definition of, XXIV, 3
, Howe's definition of, XXIV, 3
, Mellor's definition of, XXIV, 3
Condensers, A, 21
Cooling and heating curves of iron and steel, VII, 10 to 19
curves of pure metals, XXII, 1

Copper, microstructure of, I, 1
Critical points and crystallization, IX, 2, 5
dilatation, IX, 1 to 3
electrical conductivity, IX, 1
magnetic properties, IX, 3
in high carbon (hyper-eutectoid) steel, VII, 7
iron, description of, II, 6
medium high carbon steel, VII, 6; VIII, 4
pure iron, VII, 5, 10; VIII, 1
very low carbon steel, VII, 6; VIII, 3
, Carpenter and Keeling's determination of, VII, 8
, causes of, VIII, 1 to 16
, definition of, VII, 1
, determination of, VII, 10
, graphical representation of the position and magnitude of, VII, 10
, heat absorbed or evolved at, VII, 8
, influence of chemical composition on position of, VII, 5
speed of heating and cooling on, VII, 4
, instruction for detection of, VII, 19
, merging of, VII, 6, 7, 8
, minor, VII, 8
, notation, VII, 2
, occurrence of, VII, 1 to 20
, relation between structure of steel and, VIII, 12
, their effects, IX, 1 to 8
, use of neutral bodies in detecting, VII, 14
range. See critical points.
temperatures. See critical points.
Crystalline grains. See grains
growth in metals on annealing, I, 7
of strained ferrite, XII, 23 to 26
Crystallite of iron, II, 5
Crystallites, definition of, I, 2
Crystallization and critical points, IX, 2, 5
, cubic, of metals, I, 4
of austenite, X, 1 to 10
iron, II, 2
, process of, I, 1
Crystallography, systems of, I, 4
Crystals, allotrimorphic, definition of, I, 2
, cubic, of iron, II, 3, 4
, definition of, I, 1
, formation of, I, 1
, idiomorphic, definition of, I, 2
, mixed. See mixed crystals.
Cubic crystallization of iron, II, 2
metals, I, 4

D

Degrees of freedom, definition of, XXIV, 2
liberty. See degrees of freedom
Desch's types of cooling curves, VII, 18
Dilatation and critical points, IX, 1 to 3
Divariant equilibrium. See bivariant equilibrium
Double annealing treatment, XII, 8
Ductility of steel, structural composition vs., V, 17

E

Edwards on high speed steel, XVIII, 20
the hardening of steel, XV, 1, 2
Edwards' view as to the nature of martensite, XIII, 10
Electric arc lamps, A, 19 to 21
furnaces, A, 35
Electrical conductivity and critical points, IX, 1
Electrolytic iron, microstructure of, II, 1
Electromagnetic stages, A, 11
Equilibrium, bivariant, definition of, XXIV, 3
, definition of, XXIV, 1
diagram. See fusibility curves
of iron-carbon alloys, XXIII, 12 to 21
, Benedicks' diagram, XXIII, 20
, Carpenter and Keeling's diagram, XXIII, 19
, Roberts-Austen's diagrams, XXIII, 17
, Roozeboom's diagram, XXIII, 17
, Rosenhain's diagram, XXIII, 20
, the author's early diagram, XXIII, 16
, metastable, definition of, XXIV, 2
, stable, definition of, XXIV, 2
, univariant, definition of, XXIV, 3
, unstable, definition of, XXIV, 2
, unvariant, definition of, XXIV, 3
Etching, III, 6; Appendix I, 10
figures. See etching pits
of cementite, V, 7; XIX, 4
pits, formation of, I, 4
in iron, II, 3
with ammonium oxalate, V, 7
nitric acid, III, 7
picric acid, III, 6
sodium picrate, V, 7
Eutectic alloys, I, 5, 6
, constitution and occurrence of, XXII, 12 to 21
, definition of, XXII, 12
, iron-carbon, XXIII, 2
Eutectoid, definition of, IV, 3
steel, definition and structure of, V, 4
Ewing and Rosenhain, straining of iron by, II, 11
Ewing and Rosenhain's theory of crystalline growth of metals on annealing, I, 7
Eye-pieces, A, 3

F

Ferrite, crystalline growth of, XII, 23 to 26
, definition of, II, 4
, free, IV, 4
in cast iron, XIX, 1 to 10
low carbon steel, IV, 2
wrought iron, III, 1
grains, II, 1
, orientation of, II, 2
Ferro-ferrite, II, 4
Fibers in wrought iron, III, 2
Finishing temperatures, influence on the structure and properties of steel of, XI, 3

Free cementite, definition of, V, 5
ferrite, IV, 4
Furnaces, A, 35
Fusibility curves of alloys, XXII, 5 to 21
iron-carbon alloys, XXIII, 1 to 21

G

Gamma iron, VIII, 1, 14; IX, 8
, crystallization of, II, 7
, description of, II, 6
theory of the hardening of steel, XV, 2
, twinning in, II, 7
Ghost lines in steel, VI, 10
Gold, microstructure of, I, 1
Grading of steel vs. its carbon content, IV, 1
Grain refining treatment, XII, 8
Grains, crystalline orientation of, I, 3
, ferrite, II, 1
, orientation of, II, 2
, growth of, on annealing, I, 7
of metals, definition and formation of, I, 3
, heterogeneousness of, I, 3
Graphitic carbon, factors influencing formation of, XIX, 1
in cast iron, XIX, 1, 2, 3
Graphitizing of cementite, XII, 15; XXI, 1; XXIII, 7
in malleablizing cast iron, XXI, 1
Gray cast iron, XIX, 8
vs. malleable cast iron, XXI, 7
Grenet on the hardening of steel, XV, 1, 5
Guillaume on nickel steel, XVIII, 5
Guillet on case hardening, XVI, 3, 4, 5
chrome steel, XVIII, 14
manganese steel, XVIII, 5
nickel steel, XVIII, 1
silicon steel, XVIII, 15
the hardening of steel, XV, 1, 4
tungsten steel, XVIII, 12
vanadium steel, XVIII, 15, 17
Guillet's theory of special steels, XVII, 1
Gutowsky on the equilibrium diagram of iron-carbon alloys, XXIII, 20

H

Hadfield steel, XVIII, 10
Hard castings, XXI, 2
Hardened and tempered steel, microstructure of, XIV, 7
Hardening and tempering in one operation, XIII, 20; XIV, 2
carbon, definition of, XIV, 8
theory of the hardening of steel, XV, 4
, cooling for, XIII, 1
, heating for, XIII, 1
of steel, XIII, 1 to 21
, theories of, XV, 1 to 7
, structural changes on, XIII, 2
theories of the hardening of steel, classification of, XV, 1
Hardenite, definition, occurrence, and properties of, XIII, 15
Heat tinting, Appendix I, 11

Heat treatment of case hardened articles, XVI, 6
iron, influence of, II, 10
metals, influence of, I, 7
Heating and cooling curves of iron and steel, VII, 10 to 19
Heræus electric furnace, A, 35
Heyn on decrease of hardness in tempering, XIV, 9
heat liberated on tempering steel, XIV, 9
osmondite, XIV, 6
the condition of carbon in hardened and tempered steel, XIV, 8
equilibrium diagram of iron-carbon alloys, XXIII, 20
structure of hardened and tempered steel, XIV, 7
High-speed steel, XVIII, 17 to 20
, composition of, XVIII, 18
, discovery by Taylor and White of, XVIII, 18
, microstructure of, XVIII, 18
, properties of, XVIII, 17
, theory of, XVIII, 18
, treatment of, XVIII, 17, 18
Hot working, influence on structure and properties of steel of, XI, 1 to 7
Howe on tempering colors, XIV, 1
the burning of steel, XII, 17
hardening of steel, XV, 1
Humfrey and Rosenhain. See Rosenhain and Humfrey
Hyper-eutectoid steel, definition and structure of, V, 4
Hypo-eutectoid steel, definition and structure of, V, 4

I

Idiomorphic crystals, definition of, I, 2
Illuminating objectives, A, 17
Illumination for microscopical work, A, 14 to 22
, oblique, A, 14 to 16
, vertical, A, 14 to 18
Illuminators, vertical, A, 14, 16 to 18
Impurities in cast iron, XX, 1 to 10
, influence on iron of, II, 10
in metals, influence of, I, 5
steel, VI, 1 to 12
, segregation of, VI, 10
Ingot iron, II, 1
Ingotism, X, 5
Intercrystalline brittleness, XII, 27
Intergranular brittleness, XII, 27
Invar (nickel steel), XVIII, 5
Inverted microscope, A, 28
Iris diaphragms, A, 7
Iron, affinity for carbon of, XVI, 1
, allotropy of, II, 4; VIII, 1, 14
, alpha, VIII, 1, 14; IX, 8
, description of, II, 6
, beta, VIII, 1, 11, 14; IX, 8
, description of, II, 6
-carbon alloys, equilibrium diagram of, XXIII, 12 to 21
, fusibility curves of, XXIII, 1 to 21
, phase rule applied to, XXIV, 6 to 8
, structural composition immediately after solidification of, XXIII, 3
eutectic, XXIII, 2

Iron, cementation of, XVI, 1 to 6
-cementite fusibility curve, XXIII, 1
, cooling and heating curves of, VII, 10 to 14
, critical points of, VII, 5, 10; VIII, 1
crystallite, II, 5
, crystallization of, II, 2
, cubic crystals of, II, 3, 4
, electrolytic, microstructure of, II, 1
, etching in hydrogen, II, 10
pits in, II, 3, 4
, gamma, VIII, 1, 14; IX, 8
, description of, II, 6
-graphite fusibility curve, XXIII, 7
, influence of chromium on critical points of, XVIII, 13
heat treatment of, II, 10
impurities on, II, 10
mechanical treatment of, II, 11
nickel on dilatation of, XVIII, 5
tungsten on critical points of, XVIII, 12
, microstructure of, II, 1
oxide in steel, VI, 8
, slip bands in, II, 11
, straining of, II, 10, 11
sulphide in steel, VI, 3
Irreversible steels, XVIII, 2
Isomorphous mixtures, definition of, I, 5

K

Kourbatoff's etching to color cementite, V, 7
Kroll, etching of pure iron in hydrogen by, II, 9

L

Le Chatelier, André, on the hardening of steel, XV, 1, 5
Le Chatelier on the hardening of steel, XV, 1, 4
thermo-electric pyrometer for the determination of critical points, VII, 10; A, 30
Le Chatelier's view of the nature of martensite, XIII, 10
Ledebur's temper carbon, XXI, 1
Lieberkühn, A, 14
Lights for microscopical work, A, 14 to 22
Liquidus, definition of, XXII, 4

M

Magnetic properties and critical points, IX, 3
specimen holders, A, 9, 11
Malleable cast iron, XXI, 1 to 8
, annealing for the manufacture of, XXI, 3
, packing materials for the manufacture of, XXI, 3
vs. gray cast iron, XXI, 7
Castings. See malleable cast iron
Manganese in cast iron, influence and occurrence of, XX, 2
steel, VI, 5
oxide in steel, VI, 8
steel, XVIII, 5 to 12
, austenitic, XVIII, 10
, martensitic, XVIII, 10

Manganese steel, pearlitic, XVIII, 8
, properties of austenitic, XVIII, 11
, treatment of austenitic, XVIII, 11
, water-toughening of, XVIII, 11
sulphide in steel, VI, 3
Marble, twinnings in, II, 7
Martensite, Arnold's view as to the nature of, XIII, 10
, definition, description, occurrence, properties, etching, and structure of, XIII, 10
, Edwards' view as to the nature of, XIII, 10
, Le Chatelier's view as to the nature of, XIII, 10
, Osmond's view as to the nature of, XIII, 10
Martensitic special steels, XVII, 7, 9
steel, tempering of, XIV, 5
Matweieff's etching to color cementite, V, 7
method of etching slag in wrought iron, III, 3
Maurer, production of austentite by, XIII, 5
Mechanical refining, XI, 9
stages, A, 3, 12
treatment of iron, influence of, II, 11
steel, XI, 1 to 10
Metalloscope, universal, A, 10 to 13, 28
Metals, cooling curves of, XXII, 1
, crystalline growth on annealing, I, 7
, crystallization of, I, 1
, cubic crystallization of, I, 4
, definition and formation of grains of, I, 3
, influence of heat treatment, I, 7
mechanical treatment of, I, 8
, latent heat of solidification of, XXII, 2
, phase rule applied to, XXIV, 4
, solidification of, XXII, 1
Metallic alloys. See alloys
, constitution of, XXII, 1 to 21
Metarals, definition of, XIII, 18
Metastable equilibrium, definition of, XXIV, 2
Meteorites, microstructure of, X, 6 to 10
Microscopes and accessories, A, 1 to 30; Appendix I, 16 to 30
, inverted, A, 28
Microstructure of cast steel, X, 1 to 10
electrolytic iron, II, 1
hardened and tempered steel, XIV, 7
high carbon steel, V, 4,
sulphur steel, VI, 12
vs. low phosphorus steel, VI, 11
impure gold, I, 6
low carbon steel, IV, 2
medium high carbon steel, V, 1
meteorites, X, 6 to 10
oxidized Bessemer metal, VI, 12
pure copper, I, 1
gold, I, 1
iron, II, 1
metals, I, 1
platinum, I, 3
worked steel, XI, 1 to 10
wrought iron, III, 1, 2
Mixed crystals, definition of, I, 6

Monovariant equilibrium. See univariant equilibrium
Mottled cast iron, XIX, 10
Mounting samples, Appendix I, 12 to 15

N

Nachet illuminating objectives, A, 17
prism vertical illuminator, A, 17
Nernst lamp, A, 20
Neutral bodies for the detection of critical points, VII, 14
Nickel, influence of, on critical points of iron, XVIII, 2
dilatation of iron, XVIII, 5
steel, XVIII, 1 to 5
, austenitic, XVIII, 5
, case hardening of, XVIII, 4
, critical points of commercial, pearlitic, XVIII, 2
, hardening and annealing of, XVIII, 4
, martensitic, XVIII, 5
, pearlitic, XVIII, 2
, properties of pearlitic, XVIII, 3
Nitric acid etching, III, 7
Non-variant equilibrium. See unvariant equilibrium

O

Objectives, A, 3
Oblique illumination, A, 14 to 16
Orientation of crystalline grains, definition of, I, 3
ferrite grains, II, 2
Osmond on the hardening of steel, XV, 1, 2
, production of austenite by, XIII, 4
Osmond's view of the nature of martensite, XIII, 10
Osmondite, definition, description, and occurrence of, XIV, 5
Oxalate of ammonium etching, V, 7

P

Parabolic reflector, A, 14
Pearlite, carbon content of, V, 8
, definition and description of, IV, 3; VIII, 7
, formation of, X, 1 to 10
in high carbon steel, V, 4
low carbon steel, IV, 3
, varieties of, XII, 15
Pearlitic special steels, XVII, 6, 8
Phase rule applied to alloys, XXIV, 3 to 8
iron-carbon alloys, XXIV, 6 to 8
metals, XXIV, 4
, definition of, XXIV, 3
, enunciation and explanation of, XXIV, 1 to 4
Phosphorus in cast iron, influence and occurrence of, XX, 2
steel, VI, 2
Photomicrographic cameras, A, 22 to 28
Photography. See photomicrography
Photomicrography, IV, 6
Picrate of sodium etching, V, 7
Picric acid etching, III, 6
Pits. See etching pits
Planes of cleavage. See cleavage
Platinite (nickel steel), XVIII, 5
Platinum, microstructure of, I, 3

Point of recalescence. See recalescence point.
Polishing, III, 4; Appendix I, 1 to 9
machines, A, 28; Appendix I, 4 to 9
Polyhedric special steels, XVII, 1, 7
Polymorphism. See allotropy
Preserving samples, Appendix I, 12
Prism vertical illuminator, A, 16, 17
Pseudomorphism, definition of, XIV, 7
Pure metals, microstructure of, I, 1
, crystallization of, I, 1
Pyrometer, Le Chatelier thermo-electric, for the determination of the critical points, VII, 10; A, 30
Pyrometers, A, 30
, self-recording, VII, 18; A, 33, 34

Q

Quenching in annealing, XII, 6
Quaternary steels, XVII, 10. See also special steels
vanadium steels, XVIII, 17

R

Recalescence point, description and occurrence of, VII, 1
Refining, mechanical, XI, 9
Retardations. See critical points
Reversible steels, XVIII, 3
Retention theories of the hardening of steel, XV, 1
Roberts-Austen on the hardening of steel, XV, 1, 2
Roberts-Austen's equilibrium diagrams of iron-carbon alloys, XXIII, 17
use of neutral bodies for detecting critical points, VII, 14; A, 35
Robin, production of austenite by, XIII, 5
Roozeboom's equilibrium diagram of iron-carbon alloys, XXIII, 17
Rosenhain and Ewing. See Ewing and Rosenhain
Humfrey, straining of iron by, II, 10
Rosenhain's equilibrium diagram of iron-carbon alloys, XXIII, 20

S

Saladin self-recording pyrometer, A, 33
Saladin's cooling and heating curves of steels, VII, 15, 16
Segregation of impurities in steel, VI, 10
Self-hardening steel, XVIII, 13
-recording pyrometers, VII, 18; A, 33, 34
Silicates in steel, VI, 8
Silicon in cast iron, influence and occurrence of, XX, 1
steel, VI, 1
steel, XVIII, 15
Slag in wrought iron, III, 2
, composition of, III, 3
Matweieff's method of etching, III, 3
, microstructure of, III, 3
Slip bands, description and production of, II, 10
in iron, II, 11
Sodium picrate etching, V, 7
Solid solutions, XXII, 4 to 9
, definition of, I, 5
Solidus, definition of, XXII, 4
Solution theories of the hardening of steel, XV, 2

Sorbite, definition, description, and formation of, XI, 6; XII, 5; XIII, 13
Sorby-Beck parabolic reflector, A, 16
Special steels, XVII, 1 to 10; XVIII, 1 to 20
, austenitic, XVII, 7, 9
, cementitic, XVII, 1, 8, 9
constitution, properties, treatment, and uses of most important types, XVIII, 1 to 20
, definition and general character of, XVII, 1 to 10
, influence of special elements on position of critical range in, XVII, 3
, martensitic, XVII, 7, 9
, pearlitic, XVII, 6, 8
, polyhedric, XVII, 1, 7, 9
, treatment of, XVII, 8
Specimen holders, A, 7 to 9
Spheroidizing of cementite, XII, 14
Stable equilibrium, definition of, XXIV, 2
Stages, electromagnetic, A, 11
, mechanical, A, 3, 12
Stead on phosphorus in cast iron, XX, 3 to 7
the brittleness of low carbon steel, XII, 26
crystalline growth of very low carbon steel, XII, 23
Steadite, definition and description of, XX, 3
Stead's brittleness, XII, 28
Steel, annealing of, XII, 1 to 30
, temperatures of, XII, 2
, brittleness of low carbon, XII, 26
, calculation of structural composition of, V, 8 to 12; VI, 6, 7
, carbon in, IV, 3
, case hardening of, XVI, 1 to 6
castings, annealing of, XII, 13
, causes of critical points in, VIII, 1 to 16
, cementation of, XVI, 1 to 6
, chemical tests for the detection of sulphur in, VI, 4, 5
vs. structural composition of, VI, 6
, chrome, XVIII, 13 to 15
-nickel, XVIII, 16
, constitution, properties, treatment, and uses of most important types of special, XVIII, 1 to 20
, cooling and heating curves of, VII, 10 to 19
, ductility vs. structural composition of, V, 17
, eutectoid, definition and structure of, V, 4
, effects of critical points in, IX, 1 to 8
, formation of graphite in high carbon, XII, 15
, ghost lines in, VI, 10
, hardening of, XIII, 1 to 21
, high carbon, cementite in, V, 4
, microstructure of, V, 4
, pearlite in, V, 4
-speed, XVIII, 17 to 20
, hyper-eutectoid, definition and structure of, V, 4
, hypo-eutectoid, definition and structure of, V, 4
, impurities in, VI, 1 to 12
, influence of cold working on the structure and properties of, XI, 8
finishing temperatures on the structure and properties of, XI, 3
hot working on the structure and properties of, XI, 1 to 7
, iron oxide in, VI, 8
sulphide in, VI, 3
, irreversible, XVIII, 2

Steel, low carbon, etching of, IV, 6
, ferrite in, IV, 2
, microscopical examination of, IV, 6
, microstructure of, IV, 2
, pearlite in, IV, 3
, vs. wrought iron, IV, 1
, manganese, XVIII, 5 to 12
in, VI, 5
oxide in, VI, 8
sulphide in, VI, 3
, maximum strength of, V, 17
, mechanical treatment of, XI, 1 to 10
, medium high carbon, pearlite in, V, 1
, microstructure of, V, 1
, microstructure of high vs. low phosphorus, VI, 11
sulphur, VI, 12
, nickel, XVIII, 1 to 5
, normal structure of, IV, 1
, occurrence of critical points in, VII, 1 to 20
of maximum hardening power, XIII, 20
, phosphorus in, VI, 2
, physical properties of constituents of, V, 14
, production and structure of burnt, XII, 17 to 20
, relation between structure and critical points of, VIII, 12
above and below the critical range of, XII, 20
, reversible, XVIII, 3
, segregation of impurities in, VI, 10
, self-hardening, XVIII, 13
, silicates in, VI, 8
, silicon, XVIII, 15
in, VI, 1
, special, XVII, 1 to 10; XVIII, 1 to 20
, structural changes on cooling in, VIII, 5 to 16
, structure of cast, X, 1 to 10
worked, XI, 1 to 10
, sulphur in, VI, 2
, tenacity vs. structural composition of, V, 15
, tempering of hardened, XIV, 1 to 10
, theories of hardening of, XV, 1 to 7
, tungsten, XVIII, 12, 13, 17
, vanadium, XVIII, 15, 17
vs. carbon content, grading of, IV, 1
Straining, crystalline growth after, I, 7, 8
of iron, II, 11
Stress theories of the hardening of steel, XV, 5
Structural composition of alloys, XXII, 15 to 20
cast iron, calculation of, XIX, 5, 10 to 13; XX, 7 to 9
iron-carbon alloys immediately after solidification, XXIII, 3
steel, calculation of, V, 8 to 12; VI, 6, 7
Subcarbide theory of the hardening of steel, XV, 4
Sulphur, allotropy of, II, 6
in cast iron, influence and occurrence of, XX, 1
steel, VI, 2
, chemical tests for the detection of, VI, 4, 5

T

Taylor and White's discovery of high-speed steel, XVIII, 18
Temper carbon, XXI, 1
Temperatures for annealing steel, XII, 2
Tempering and the retention theories of the hardening of steel, XV, 6
stress theory of the hardening of steel, XV, 6
colors, XIV, 1
, decrease of hardness on, XIV, 9
, explanation of, XIV, 2
, heat liberated on, XIV, 9
, influence of rate of cooling in, XIV, 2
time in, XIV, 1
of austenitic steel, XIV, 3
case hardened steel, XVI, 6
hardened steel, XIV, 1 to 10
martensitic steel, XIV, 5
troostitic steel, XIV, 5
temperatures, XIV, 1
Tenacity of steel, structural composition vs., V, 15
Ternary steels, XVII, 1. See also special steels
Thermal critical points. See critical points
treatment. See heat treatment
Toughening treatment, XII, 8
Transformation points. See critical points
range. See critical points
Transition constituents. See also martensite, troostite, and sorbite
, definition and formation of, XIII, 15, 17
Troostite, Arnold's view as to the nature of, XIII, 12
, Benedicks' view as to the nature of, XIII, 12
, definition, description, occurrence, properties, etching, and structure of, XIII, 11
Troostitic steel, tempering of, XIV, 5
Troosto-sorbite, XIII, 15
Tschernoff iron crystallite, II, 5
Tungsten, influence on the critical points of iron of, XVIII, 12
steel, XVIII, 12, 13
Twinnings, definition of, II, 7
in brass, II, 7
gamma iron, II, 7
marble, II, 7
produced by pressure, II, 7

U

Univariant equilibrium, definition of, XXIV, 3
Universal metalloscope, A, 10 to 13, 28
Unstable equilibrium, definition of, XXIV, 2
Unvariant equilibrium, definition of, XXIV, 3

V

Vanadium steel, XVIII, 15, 17
Vertical illumination, A, 14 to 16
illuminators, A, 14, 16 to 18

W

Water-toughening of manganese steel, XVIII, 11
Welsbach lamp, A, 19
Widmanstätten structure, X, 6

White, Maynard. See Taylor and White
White ware, XXX. 3
  brass castings, XXX. 4
    annealing for, XXX. 4
Wrought iron, composition of, III. 1
  . defects of, III. 1
  . fibre in, III. 2
  . mechanical properties of specimens of, III. 7
  . structure of, III. 1, 2
  . slag in, III. 2
  . to join various steels, IV. 1

Z

Zeiss prism Binoculars, A. 17